

*Saunders' International Student Edition*

# GENERAL CHEMISTRY

## *Inorganic and Organic*



GARTH L. LEE, Ph.D.  
HARRIS O. VAN ORDEN, Ph.D.

540  
Lee

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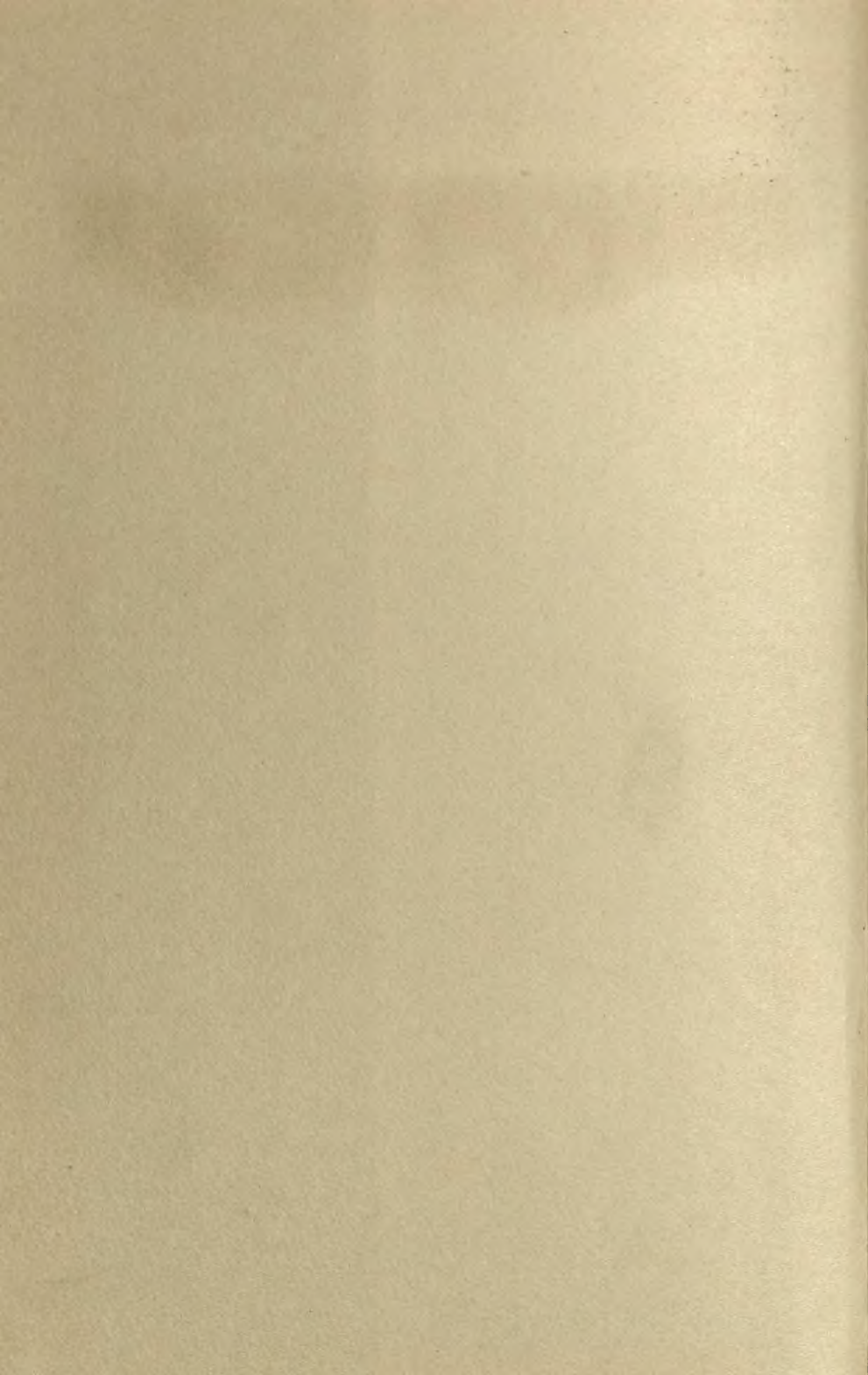
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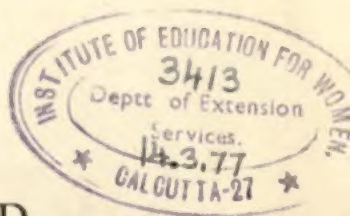






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**GENERAL  
CHEMISTRY**  
Inorganic and Organic



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**Second Edition**

**Illustrated by Larry E. Elsner and R. E. Bird**

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## General Chemistry

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# Preface to the Second Edition

THE AUTHORS have made this revision one of correction, modernization and addition. Many details have been investigated with respect to accuracy and teachability and all suggestions received have been considered and many changes made.

The modernization is four-fold. (1) The section on the noble gases has been expanded to include the preparation and properties of the newly discovered compounds. (2) Modern atomic orbital notation ( $1s^2 2s^2 2p^6$  etc.) has been added and integrated into the discussion of atomic structure. (3) Sigma and pi bonding have been treated along with covalent bonding. The new concepts are employed to illuminate the reactions taking place among unsaturated and aromatic organic compounds. (4) The oxidation potentials have been changed in sign to agree with modern usage. Necessary changes have been made in related discussions.

Three completely new chapters have been added: Chapter 24, "Colloids"; Chapter 27, "The Nucleus and Chemistry"; and Chapter 40, "Biochemistry, an Introduction." It is hoped that the inclusion of these chapters will satisfy the needs of those who expressed an interest in one or more of the three fields. These chapters may be included in the course or left out without destroying the continuity of the text.

Our sincere thanks are extended to all who offered either suggestions or criticism and to Mr. Richard E. Bird who prepared the new illustrations included in this edition.

GARTH L. LEE  
HARRIS O. VAN ORDEN

## Preface to the Second Edition

The authors have made the revision one of correction, amplification and addition. Many details have been investigated with respect to accuracy and consistency and all suggestions received have been considered and many changes made.

The modification is twofold. (1) The section on the noble gases has been expanded to include the properties and properties of the newly discovered compounds. (2) Modern atomic orbital notation ( $sp^2$ , etc.) has been added and integrated into the discussion of atomic structure. The  $sp^2$  and  $sp^3$  hybrid orbitals have been treated along with covalent bonding. The new concepts are employed to illustrate the structure of the various types of compounds and organic compounds. (3) The section on chemical equilibrium has been expanded to include the study of the various types of chemical equilibrium and the study of the various types of chemical equilibrium.

The authors have also made a few minor changes in the chapter on "Chemical Equilibrium" and "Chemical Equilibrium" and "Chemical Equilibrium". It is hoped that the revision will be of interest to those who are interested in the study of the various types of chemical equilibrium and the study of the various types of chemical equilibrium. The authors are grateful to the many who have given the new edition included in this edition.

LESLIE J. GILBERT  
HAROLD O. VAN COTT



# Preface to the First Edition

THERE IS NO natural starting point for the study of chemistry. The fundamental concepts of chemistry are similar to the elements of a circle—each element both precedes and succeeds every other. To understand one phase of chemistry fully one must understand the others; hence the student must traverse the circle many times. In this text an attempt is made to begin discussion at points where the student has (in his own experience) already broken into the circle. The familiar position is examined and described before proceeding to the unfamiliar. Such an approach must have certain virtues, for this is the method followed by those who contributed to the formulation of the science.

The subject matter falls into three natural, unmarked divisions. Chapters 1 to 7 present general definitions of chemistry and matter. The characteristics of matter are indicated, and the tools used to evaluate them are discussed. Matter is viewed in its gross structure as it appears to all. It is then reduced, step-by-step, through mixtures and compounds to elements and through mixtures to molecules and atoms. A brief study of the elements reveals likenesses and differences enabling one to understand the arrangement of the Periodic Table. A study of the atomic structure describes the nature of the forces that bond atom to atom and molecule to molecule to form aggregates visible to the naked eye.

Chapters 8 to 28 constitute a more extensive description of the elements. They are studied in groups as they appear in the periodic table, with the more common elements described specifically as examples of the groups they represent. Interspersed among the descriptive chapters are others dealing with the principles and theory necessary for the description.

Chapters 29 to 40 introduce organic chemistry, the chemistry of carbon, as it appears with some few other elements in an endless variety of compounds.

These compounds are discussed by functional groups; for example, alkanes, alkenes, alkynes, ethers, alcohols. Included is a description of the appearance and functions of more complicated components of petroleum, fibers, drugs and living organisms.

Certain topics are covered more completely than is usual in an introductory text, to the exclusion of others. We feel that a more thorough knowledge of a few topics is preferable to a superficial treatment of many.

The necessary mathematics has been presented in such a way that the student must think through the solution. Memorization and routine application of formulas for problem-solving are discouraged.

We acknowledge assistance received both directly and indirectly from many individuals. Among these are Professors Melvin C. Cannon, Lowell G. Tensmeyer, G. Olof Larson and Jack Spence, who used a prepublication issue of a portion of the text, with all its typographical and pedagogical errors, and Professors Sherwin Maeser, Norman Bauer and Calvin Vanderwerf, who read portions and offered helpful suggestions. Especial acknowledgement is due Mr. Larry Elsner, whose illustrations appear throughout the volume. We are grateful also to the Utah State University Research Council for financial assistance in preparing the manuscript and illustrations.

GARTH L. LEE

HARRIS O. VAN ORDEN



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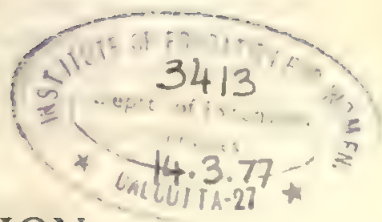
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## INTRODUCTION

Chemistry is a study of the behavior of matter. It is concerned especially with those changes in the composition of matter that are called chemical reactions, with the heat effects associated with these changes and with the factors that control them. The importance of these chemical changes has taken either the chemist or methods developed by him into a great many vocational fields.

Chemistry is concerned with a variety of things. The changes that occur within a dye when a colored fabric fades; the formation of acrolein in frying bacon; the charring of wood in sulfuric acid; the setting of concrete; the rusting of iron; the vulcanization of rubber; photosynthesis; the energy released in animal metabolism; deterioration of lubricating oils; reactions occurring at nerve endings, and the heat released in the burning of coal—all these are chemical reactions.

Chemical plants produce soap, paint, sulfathiazole, D.D.T., TNT, plastic tubing, rubber, nylon, Dacron, fingernail polish, food flavors, ethyl alcohol, aspirin, imitation leather, detergents, hydrogen peroxide, soil conditioners, antioxidants to preserve butter, plastic tile, fly spray and many other products. The analysis of uranium ores, the developing of photographic film, the melting of ice on the streets, the waterproofing of clothing, the reduction of iron oxide to iron and the bleaching of hair are chemical processes.

Some study chemistry to become chemists. A chemist may make chemicals; he may pursue research to develop new chemicals or improve the old; he may make analyses to test the quality of a product; he may be a consultant in a metallurgical laboratory; he may test the effects of new drugs on guinea pigs; or he may be hired by the public health department to analyze the air for impurities.

Many study chemistry to learn the nature of the physical world. The student of chemistry soon learns of the similarities that exist in the myriad forms of matter. He learns of the marvelous order of physical things and of the immutability of natural law. All these help man to be at home in the world in which he lives. This is a chemical age. One with no conception of chemical changes can know little of life.

## CHEMISTRY IS A SCIENCE

A science is a field of study or investigation in which the scientific method is employed. The scientific method is a system of attacking a problem in which careful accurate observation and vivid yet thoughtful imagination are the two major factors. In principle the problem-solving strategy may be separated into four phases:

1. Facts are discovered by quantitative observation of the behavior of a system, and the facts are recorded.

2. The observed facts are correlated or generalized in the statement of a law. Quite often the law is mathematical in nature.

3. The question is considered, "Why is this a law?" A mental picture is evolved to explain the observed behavior. This picture is called a theory.

4. Once the theory is accepted, one sees that not only will the picture explain the workings of the law or laws that conceived it, but it will predict certain other relationships. These are checked by experiments which either agree with and expand the theory or prove it false. If the theory is disproved, new theories and experiments follow, with the scientist holding to the best and simplest picture until a better one is found. The scientific approach will be exemplified later when the development of the fundamental theories is considered.

The scientific method has been extremely fruitful in the physical sciences. Its development and application is in a large measure responsible for the great technological advancement of this age. It is proving to be useful in other fields, such as sociology, economics and psychology. A mastery of this method and an ability to use it to solve other problems is in itself an excellent reason for studying chemistry.

It is obvious that science by its nature has definite limitations. It is limited to observations of either naturally occurring or staged phenomena. Science thrives when observations are quantitative and exact. Because the theories must be tested by observations, advancement is slow. Scientific truth is not absolute, but becomes more and more sure as experimental evidence is accumulated.

Chemistry is very closely related to physics. Both are studies of matter. But physics has, in general, a different emphasis from that of chemistry. Physics is a study of matter in relation to the energy it possesses by virtue of its position or motion; its heat-conducting properties; its electrical properties; and its relationship to the transmission of light, sound and heat. Despite the different emphasis, certain areas of study are common to both



and necessary to an understanding of either. Material will be drawn from physics when necessary.

Mathematics is a necessary tool for expressing the quantitative relationships found in chemistry. Extended studies in chemistry require a more extensive knowledge of mathematics but, in this course, a fundamental knowledge of college algebra and a reasonable facility in working so-called "story problems" will suffice.

## CHAPTER 2

# MATTER

The physical world about us is composed of matter. The books you read, the food you eat, the records you play, your automobile—all are material. The thoughts expressed in this book, the satisfied feeling you have when you view your dinner, the music that comes from the record, and the feeling of power you have when you press on the accelerator are real, but they are not material.

### CHARACTERISTICS OF MATTER

If something is colored, if it has an odor, if it is hard (or soft), if it is hot (or cold), it is composed of matter. Anything that can be detected by any one of the five senses is material. However, not all samples of matter have all the above properties, nor can all samples of matter be detected by one of the senses. Two characteristics are common to all portions of matter: all occupy space and all possess mass. Either of these is a sufficient criterion for matter, because anything that possesses mass must occupy space, and vice versa. Things not material meet neither requirement.

The *volume* possessed by a sample of matter may be varied, sometimes drastically, but it can never be eliminated entirely. A large volume of air may be compressed into a football or an automobile tire, but an attempt to add an unlimited amount will result in bursting the container.

### MEASUREMENT OF MATTER

The *space* or *volume* occupied by matter may be measured *quantitatively* in any of several arbitrary units or dimensions. The pint, the cubic foot, the gallon, the teaspoon and the bushel are all units of volume. These are seldom used in courses in chemistry; instead units of the *decimal system* are used, because they are more easily adapted to computation.

## THE DECIMAL SYSTEM

**Units of Length.** The basic unit of length in the metric system is the meter. The length of the meter stick is just about 39.4 inches (Fig. 2.1). Other units are derived by dividing or multiplying the meter by 10, 100 or 1000, etc. Units of length are summarized below.

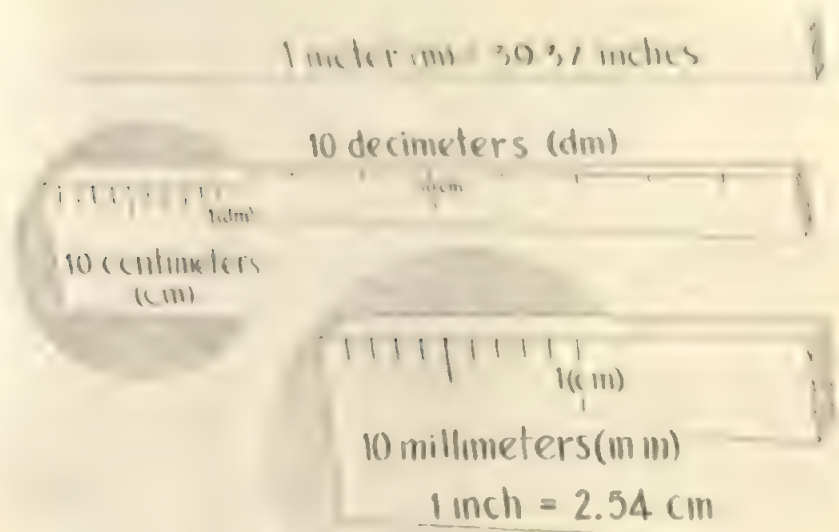


Figure 2.1. The meter stick.

1 kilometer (km)	= 1000 meter	$\approx$ $5/8$ miles
1 meter (m)	= 1 meter	= 0.001 km $\approx$ 39.37 inches
1 decimeter (dm)	= 0.1 meter	= 0.0001 km
1 centimeter (cm)	= 0.01 meter	= 0.1 dm
1 millimeter (mm)	= 0.001 meter	= 0.1 cm
1 micron ( $\mu$ )	= 0.001 mm	= 0.0001 cm
1 millimicron (m $\mu$ )	= 0.001 $\mu$	= $1 \times 10^{-6}$ mm
1 Ångström (Å)	= 0.1 m $\mu$	= $1 \times 10^{-8}$ cm

Measurements made in the laboratory are usually of such length as to be conveniently written in meters, centimeters and millimeters; the Ångström unit is used in discussing atomic dimensions.

From the table above one can derive the following equivalents:

- a.  $0.25 \text{ m} = 0.00025 \text{ km} = 25 \text{ cm} = 250 \text{ mm}$   
 b.  $2.5 \times 10^{-3} \text{ m} = 2.5 \times 10^{-6} \text{ km} = 0.25 \text{ cm} = 2.5 \text{ mm}$

\*  $\approx$  means approximately equal to.



The change from one unit of dimension to another involves merely the moving of the decimal point, but in the English system of inches, feet, yards, rods and miles, a more difficult conversion is required.

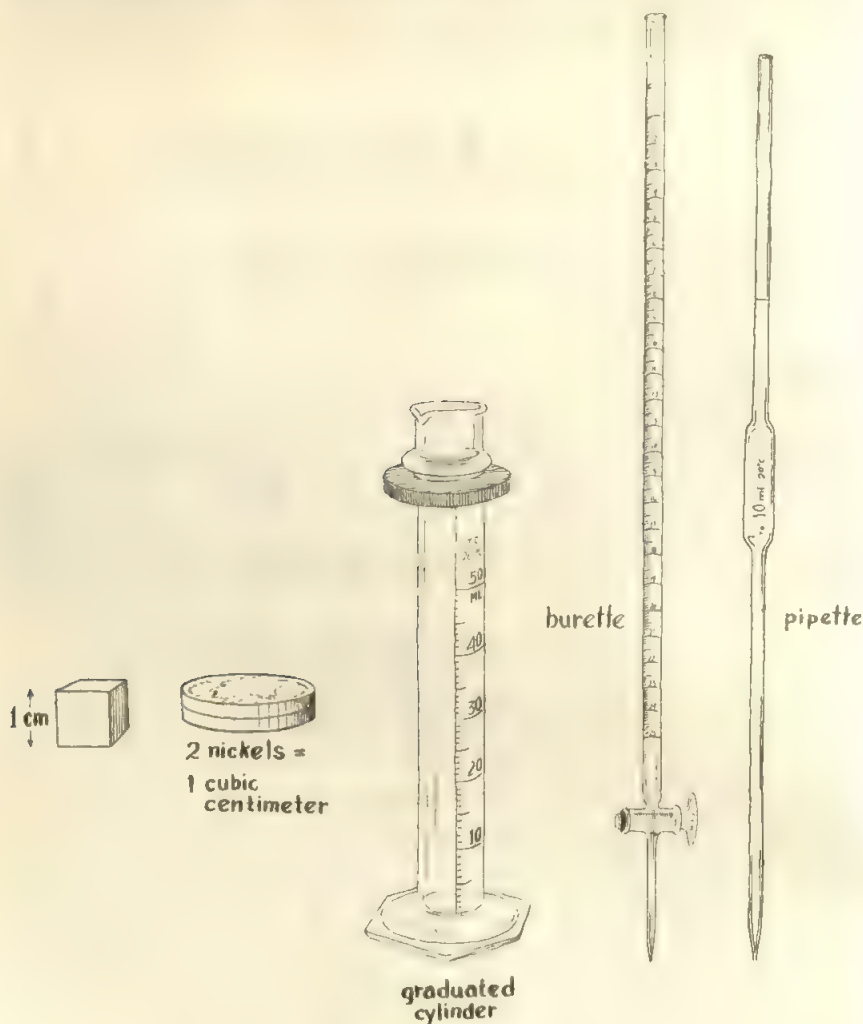


Figure 2.2. Volume apparatus.

**Units of Area.** The units of *area* in the metric system are the  $\text{cm}^2$ ,  $\text{m}^2$ ,  $\text{km}^2$ , etc. The area of a rectangle is the product of the length and width. The area of a paper 10 cm by 15 cm is  $150 \text{ cm}^2$  (150 square centimeters).

**Units of Volume.** A unit of *volume* used in the laboratory is the cubic centimeter (Fig. 2.2), written either as  $\text{cm}^3$  or cc. This is the volume of a cube  $1 \text{ cm} \times 1 \text{ cm} \times 1 \text{ cm}$ . The cubic millimeter ( $\text{mm}^3$ ) is used for micro work, but the cubic meter is much too large a unit to be useful in stating

laboratory volumes since it contains  $1 \times 10^6$ , or 1 million  $\text{cm}^3$ . An intermediate measurement between the  $\text{m}^3$  and  $\text{cm}^3$  which is used commonly in the laboratory is the liter (L). The liter is defined as the volume of 1000 grams of water measured at  $4^\circ\text{C}$ . In metric units, the liter is  $1000.027 \text{ cm}^3$ . The milliliter (ml) is one-thousandth of a liter and is almost exactly the same as the cubic centimeter. In this book they will be used interchangeably (usually the  $\text{cm}^3$  for solids, the ml for liquids).

Three pieces of glassware commonly used for measuring and dispensing measured volumes of liquids in the laboratory are the *graduated cylinder*, the *burette* and the *pipette*. The *graduated cylinder* is the chemist's measuring cup. It is made in various sizes, the total volume varying from 5 ml up to 3 L; it is used in making quick, approximate measurements.

The *burette* is a long glass tube which is mounted vertically, with graduations running from 0 at the top to the total volume in milliliters at the bottom. At the bottom is a stopcock with a glass tip. Liquid can be dispensed by opening the stopcock. The amount dispensed is indicated by the difference in the reading before and after dispensing. The burette is used when the chemist desires to add a solution slowly, even a drop at a time, while keeping account of the total amount added.

The *pipette* is a length of glass tubing with a tip on one end and usually a bulb in the center. The pipette delivers one set volume of liquid drawn up into the pipette to the mark just above the bulb (much as one draws a beverage through a straw). With the forefinger over the end of the tube one can transfer the pipette to another container, into which the liquid empties when the forefinger is removed.

**Units of Mass.** The second universal characteristic of matter is the *possession of mass*. The basic unit of mass used in scientific work is the gram. It appears with other derived units below.

kilogram (kg)	= 1000 gram	$\approx 2.2$ pounds
gram (g)	$\approx 1/454$ pound	$= 1/28.4$ ounce
milligram (mg)	= 0.001 g	
microgram ( $\mu$ )	= 0.001 mg	$= 1.0 \times 10^{-6}$ g

Consistent with the above definitions are the following equalities:

- a.  $0.37 \text{ kg} = 370 \text{ g} = 3.70 \times 10^2 \text{ mg}$
- b.  $0.00034 \text{ kg} = 0.34 \text{ g} = 340 \text{ mg}$

Again the change from one unit to another is done by moving the decimal point, the conversions being much simpler than those in the system of ounces, pounds and tons.

## THE BALANCE

Bodies of matter have an inherent attraction for one another. The attraction between two bodies is proportional to the product of their masses and inversely proportional to the square of the distance between them. In mathematical form:

$$\text{Force} = K \frac{m_1 m_2}{d^2}$$

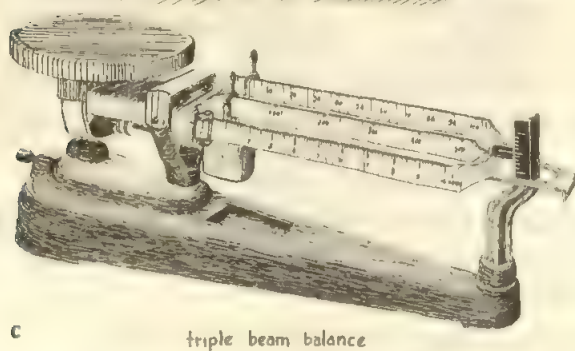
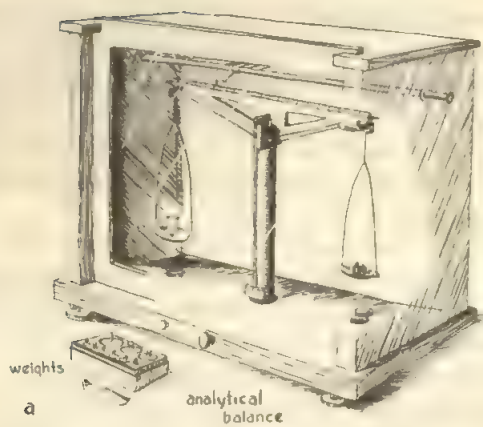


Figure 2.3. Chemical balances.



where

$m_1$  and  $m_2$  are the masses of the two bodies,  $d$  is the distance between their centers and  $K$  is a constant, its numerical value depending on the units of  $m$  and  $d$ .

This force of attraction is negligible between two objects of ordinary mass, but when one of these is the earth, with a mass of  $6.0 \times 10^{27}$  g, the force may become very great. Thus, it is easy to roll two large iron balls apart, but quite difficult to pull one from the earth's surface, that is, to lift it. One can see from the equation that when two objects are placed side-by-side, the attractive force toward the center of the earth, the gravitational force, will be proportional to the masses they possess: for in this situation all factors on the right side of the equation, except  $m_1$ , become constants. In other words, a 10-g weight will be twice as difficult to lift as a 5-g weight; it has twice the mass.

All types of scales or balances use this force of gravity in weighing, or finding the mass of objects. A 10-pound bag of potatoes stretches the spring on a grocer's scales twice as far as a 5-pound bag. The pointer on the dial rotates as the spring is lengthened.

A two pan balance is constructed like a "teeter" or "see-saw." The analytical balance and the horn pan balance (Fig. 2.3 a,b) are two examples. A metal bar is supported or suspended at the center so that it balances. Two pans of equal mass are suspended from or set on the bar, one on each end. In weighing, the object to be weighed is placed on one pan, tipping the balance arm in that direction. Weights (pieces of brass of known mass) are added, one by one, to the other pan until the bar is restored to its original horizontal position.

When the bar is horizontal each pan load is pulled with the same force; therefore, each contains the same mass. The mass of the object is found by taking the sum of the masses of the weights on the other pan.

The sliding weight balance (e.g., triple beam balance; Fig. 2.3c) uses the principle observed in a "see-saw" arrangement. A 10-g weight 10 cm from the center or point of suspension, will balance a 5-g weight 20 cm from that point on the other arm of the balance. Thus, by moving one weight back and forth on one arm of the balance, the chemist can balance objects with different masses placed on the pan on the opposite arm. A scale on the bar enables one to read the balancing mass directly.

## DENSITY

These two characteristics of matter, *mass* and *volume*, are combined in a third called density. The *density* of a substance is the mass of one unit volume of that substance and may be given in various units: g/ml, g/cm<sup>3</sup>, g/L and others. Usually the density of liquids and solids is expressed in g/ml or g/cm<sup>3</sup>, whereas gas densities are given in g/L to avoid small fractions.

Density is calculated by dividing the mass of an object by its volume.

EXAMPLE: Calculate the density of alcohol, knowing that 80 ml weighs (has a mass of) 64 g.

$$\text{Density} = 64 \text{ g}/80 \text{ ml} = 0.80 \text{ g/ml}$$

One can reason that if 64 g is distributed equally among 80 ml, one ml will contain  $1/80$  of that 64 g. One can check his answer by noting there are more milliliters than grams, and therefore there will be less than 1 g per ml. Notice that the labels g and ml appear correctly in the answer g/ml.

EXAMPLE: At  $0^{\circ}\text{C}$  and 1 atmosphere pressure, 22.4 L of oxygen gas has a mass of 32 g. Find the density in g/L.

$$32 \text{ g}/22.4 \text{ L} = 1.43 \text{ g/L.}$$

Again, 32 g is contained equally by 22.4 L; therefore, each liter contains more than 1 g, or about 1.5 g.

Density is used in several ways. Three will be discussed here.

1. Density is a *physical property*; its *numerical* value is characteristic of the material and helps to identify it. It means nothing in comparing substances to say "water weighs 1050 g and iron weighs 6000 g," but it is useful to know that 1  $\text{cm}^3$  of water weighs 1 g and 1  $\text{cm}^3$  of iron is 7.86 g. When you say that iron is heavier than water, you are comparing the weights of equal volumes and are speaking of densities. In the table below is a list of densities of some common substances in g/ml ( $\text{g}/\text{cm}^3$ ).

Alcohol .....	0.80
Water .....	1.00
Aluminum .....	2.7
Bromine .....	3.4
Iron .....	7.86
Copper .....	8.92
Silver .....	10.5
Lead .....	11.3
Mercury .....	13.6
Gold .....	19.3

2. Using density one can calculate the *mass* of a certain *volume* of *liquid*.

EXAMPLE: Concentrated sulfuric acid has a density of 1.84 g/ml. Calculate the weight of 50 ml.

$$50 \text{ ml} \times 1.84 \text{ g/ml} = 92 \text{ g}$$

Again if 1 ml is almost 2 g, 50 ml will be almost 100 g. Cancellation of units (just as you cancel numbers in fractions) gives you the correct units for your answer.

3. Using density and mass one can calculate the volume of a liquid sample.

EXAMPLE: How many ml of bromine must one take to get 56 g? The density of bromine is 3.4 g/ml.

$$56 \text{ g}/3.4 \text{ g/ml} = 16 \text{ ml}$$

If 1 ml contains more than 3 g, then one needs less than  $1/3$  as many milliliters as grams. The unit g cancels out, and ml is left in the numerator as the correct unit for the answer.

The density of a liquid may be *measured directly* with a *hydrometer* (Fig. 2.4a). The hydrometer utilizes the principle discovered by Archimedes that

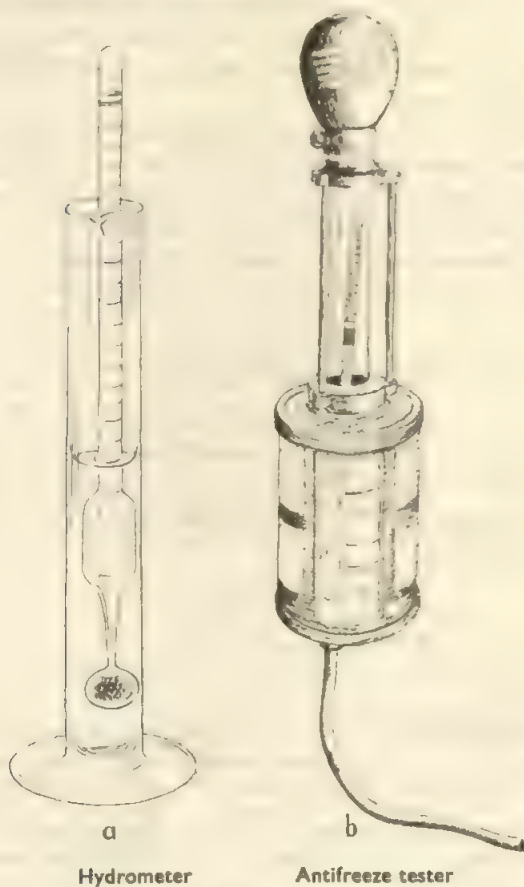


Figure 2.4.

a floating body rests down in a liquid until it displaces a volume of that liquid having a mass equal to its own. When placed in a liquid, the hydrometer floats partially submerged. The lighter the liquid (the lower its density), the greater amount must be displaced by the hydrometer and the greater the extent of submersion. If the liquid is less dense than the average density of the hydrometer, it will sink to the bottom. On the other hand, the greater the density, the higher the hydrometer floats. The hydrometer is calibrated in densities, so that one can take the reading of the hydrometer scale at the surface of the water.

Hydrometers are used to test the antifreeze solution in automobile radiators. Ethylene glycol, the major ingredient of most permanent antifreezes, is more dense than water. Addition of ethylene glycol to water gives a solution of density greater than that of water alone. The density of the solution increases and the freezing point lowers as ethylene glycol is added. The service station attendants merely draw the antifreeze solution up into the chamber containing the hydrometer. The higher it floats the greater the percentage of ethylene glycol and the lower the freezing point. Although the density is the property determined, the hydrometer is calibrated in terms of the freezing point of the solution having that density.

Although density is perhaps the only physical property possessed by all samples of matter, there are other properties possessed by some which can be measured quantitatively and which are useful in characterizing the samples. Among these are refractive index, color, odor, melting temperature, hardness, viscosity, vapor pressure and surface tension. All of these are used in various ways in chemistry. We shall discuss some of these later and use them when needed.

Table of Densities in g/ml or g/cm<sup>3</sup>\*

Ethyl alcohol	0.806 at 0°C 0.785 at 25°C
Water	1.000 at 4°C 0.997 at 25°C 0.958 at 100°C
Rock salt	2.18
Marble	2.70

Metals	Alloys
Aluminum (Al) 2.71	Aluminum bronze (90% Cu, 10% Al) 7.60
Copper (Cu) 8.92	Bell metal (78% Cu, 22% Sn) 8.70
Gold (Au) 19.30	Gold coinage (90% Au, 10% Cu) 17.17
Lead (Pb) 11.34	Magnalium (70% Al, 30% Mg) 2.00
Magnesium (Mg) 1.74	Solder (50% Sn, 50% Pb) 8.73
Tin (Sn) 7.29	

\* Data to be used in Problems 11–27.

## PROBLEMS

1. Fill in this table with equal values in the units indicated.

m	cm	mm	Å
2.71			
	.389		
		3.64	
			24.3



2. Write the following numbers in correct exponential form (a) 2700, (b) 0.0134, (c) 0.0000019, (d) 4.00043, (e)  $64 \times 10^{-3}$ .
3. Sand was spilled into 30.6 ml of water in a graduated cylinder until the total volume was 46.7 ml. How many  $\text{cm}^3$  of sand were added?
4. 9.72 g of a metal was added to 26.21 ml of water in a graduated cylinder, increasing the volume to 29.81 ml. Calculate the density of the metal.
5. A watch glass was balanced on a horn pan balance with one 10 g, one 5 g, two 200 mg and one 50 mg weight. Salt was added until the whole was balanced by one 20 g weight. Find the weight of the salt added.
6. 25 ml of concentrated hydrochloric acid weighs 34.25 g. Calculate the density of concentrated HCl.
7. Find the weight of a bar of aluminum  $1.5 \text{ cm} \times 1.5 \text{ cm} \times 15 \text{ cm}$ . The density of aluminum is 2.7 g/cc.
8. A graduated cylinder has an inside diameter of 1 cm. Calculate the distance between the 25 ml and 26 ml marks. The area of a circle is  $\pi r^2$ .
9. At 1 atm pressure and 0°C, 18 g of nitrogen occupies 14.4 liters. Calculate the density of nitrogen gas in g/L at these conditions.
10. Hydrogen gas has a density of 1/14 that of nitrogen. Find the volume of 8.0 g of  $\text{H}_2$  at 1 atm and 0°C.
11. At 0°C, 45 ml of ethyl alcohol weighs 36.3 g. Calculate the density of ethyl alcohol at 0°C.
12. What is the volume of this 36.3 g at 25°C? Answer: 46.2 ml
13. What is the weight of 46.2 ml of ethyl alcohol at 25°C?
14. 50 g of aluminum bronze is exactly 6.58  $\text{cm}^3$ . Calculate the density.
15. a. Calculate the volume of 40 g of tin. Answer: 5.48  
b. Calculate the volume of 40 g of lead. Answer: 3.52  
c. Calculate the volume of 80 g of solder. Answer: 9.16
16. Calculate the weight of a bar of gold coinage 1 cm by 0.4 cm by 15 cm. Answer: 103.0 g
17. Some gold shot was added to 32.6 ml of water in a graduated cylinder until the final volume was 34.2 ml. Calculate the weight of the gold shot. Answer: 30.8 g
18. How many  $\text{cm}^3$  of copper and how many  $\text{cm}^3$  of tin are needed to make 75  $\text{cm}^3$  of bell metal? Answer: 57.2  $\text{cm}^3$ ; 19.7  $\text{cm}^3$
19. A flask was filled level full with 554 ml of water at 4°C, then warmed to 100°C. How many g of water were lost from the flask? Answer: 23 g
20. A watch glass was balanced on a horn pan balance with the following weights: 1 10 g, 1 5 g, 2 2 g, 1 500 mg, and 1 10 mg.  
Metal filings were then added to the watch glass until a balance was struck with the following weights: 2 20 g, 2 200 mg, and 1 50 mg.  
The metal was poured carefully into a graduated cylinder containing 14.50 ml of water. The final volume was 16.96 ml. Which of the metals in the table above were the filings?
21. What is the volume of 20 g of rock salt?
22. Calculate the volume of 100 g of a 20% (by weight) solution of salt. Density is 1.15 g/ml.
23. Calculate the change in total volume when 20 g of salt is dissolved in 80 g of water.
24. a. Calculate the weight of 56 ml of a 20% salt solution.  
b. How many grams of salt are contained in the 56 ml of solution?
25. What length of an aluminum bar is equal in weight to a 30 cm magnesium bar of the same diameter?
26. A cube of zinc  $3 \text{ cm} \times 3 \text{ cm} \times 1 \text{ cm}$  weighs 64.3 g. Calculate the density of zinc.
27. Marble chips dropped into a graduated cylinder containing 32.1 ml raised the level to 39.5 ml. How many grams of chips were used?

## THE STATES OF MATTER

On the basis of differences in certain physical properties, all materials may be divided into three general classes or states. It is apparent that salt, water and air are quite different from each other. Each is an example of one of the states of matter. Salt is a *solid*; air is a *gas*; and water is a *liquid*. Each class will be discussed briefly.

## SOLIDS

True solids have one distinguishing characteristic. Each solid possesses a certain form or structure. When viewed through a microscope, table salt appears as a mass of tiny cubes and tiny boxes (more than one cube together). The individual particles appear in many sizes, but, barring accidental imperfections, all have square corners. If these cubes are crushed into still tinier particles, they are also cubes. Salt is a true solid; it has a definite structure. Attempts to change the structure of individual units are resisted by the unit or crystal to the point of its destruction.

## LIQUIDS

Liquids differ from solids in that individual units have no definite form or shape. In fact, for these reasons one can hardly speak of individual units. Because of this lack of rigid structure, liquids can flow, and consequently assume the form of a container, or of the lower portion of a container. All liquids have some resistance to flow. This resistance is known as viscosity. Some liquids such as water, alcohol and gasoline have very low viscosity, but others (molasses, lubricating oil and tar) present a great deal of resistance. This viscosity indicates that there is some transitory or temporary arrangement or structure within the liquid that must be altered as the liquid flows.

This is true, but it is not a rigid form and differs greatly from that of solids. One well-known liquid is quite often classed as a solid because of its unusually high viscosity. This liquid is glass, window glass. Investigations have shown that glass has no definite internal structure.

One property common to both solids and liquids is their resistance to change in volume by variations in temperature or pressure. They are relatively incompressible.

### GASES

Gases differ from solids in possessing no apparent structure. They differ from both solids and liquids in possessing no special volume. A gas assumes both the form and volume of its container. A gas will fill completely and almost instantaneously any space into which it is admitted. Since a sample of gas may occupy different volumes, the density of the gas will vary with that volume. In general the density of gases at room temperature and pressure is many times less than that of solids or liquids. For that reason, densities of solids and liquids are usually recorded as grams per cubic centimeter, whereas the densities of gases are given in grams per liter.

### CHANGES OF STATES

In general, under the proper conditions, a particular sample of matter may exist in each of the three states. Consider water, which is a liquid at room temperature. When cooled below  $0^{\circ}$  centigrade, water freezes into brittle, translucent ice crystals. On warming above that temperature, it is converted again to water. This same water may be converted to steam and recondensed as water. A cold spoon held over the spout of a boiling tea kettle condenses the steam to drops of water.

When water is distilled as a step in its purification, it is converted to steam and then condensed to water again. A laboratory apparatus used to accomplish this is shown in Figure 3.1. Water is boiled in the distilling flask. Steam leaves the flask through the side arm where it is cooled in the water-jacketed condenser and converted to water, which drips into the receiving flask.

Some substances thought to exist in only one or two states can be converted to other states, but only at extremely high or low temperatures. Steel and salt may be melted to a liquid and then vaporized at high temperatures. In contrast, hydrogen gas and helium gas may be liquefied and finally frozen, but only at temperatures near absolute zero. However, there are other substances which break down chemically (decompose) when heated to temperatures below their boiling point or even the melting point. Thus not all substances exist in all three states.

Changes in state are often thought to proceed progressively from solid, to liquid, to gas (vapor) and return in the exact reverse path. This is not always the case. Dry ice (solid carbon dioxide) changes directly to a gas at room temperature and pressure. A change in state from solid to vapor is known as sublimation. Thus we say that dry ice sublimates. No wet spot is left

when the ice is gone. At high pressure dry ice will melt. Carbon dioxide is shipped as a liquid in tanks. Iodine is purified by sublimation. According to one method, iodine is placed near an electric light bulb in a closed container. The iodine is vaporized by the heat of the lighted bulb and travels in the

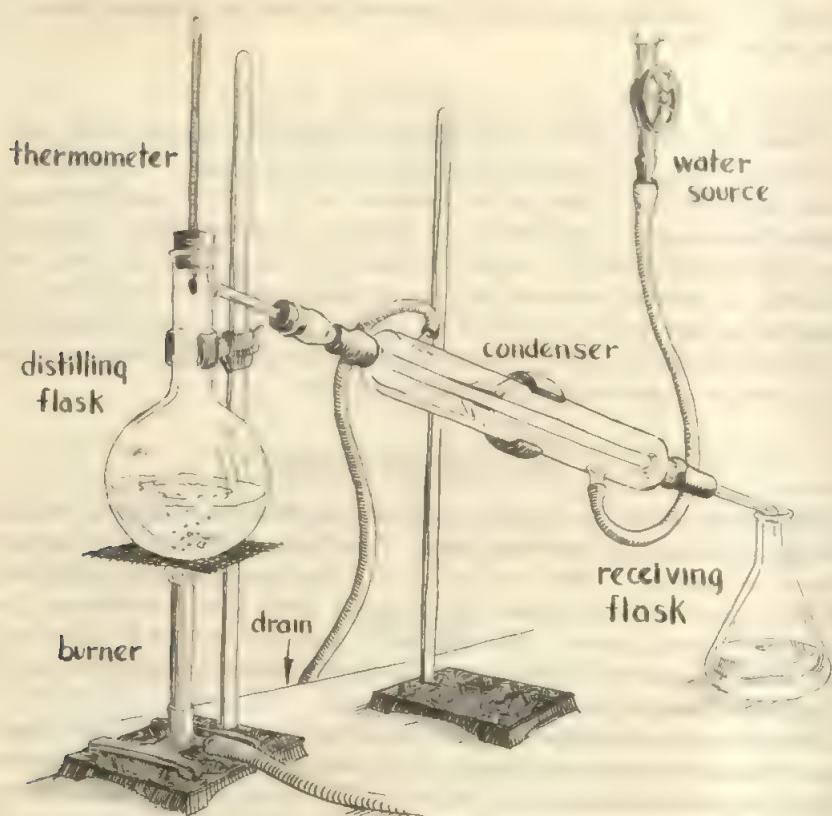


Figure 3.1. Distillation apparatus.

vapor phase to cooler spots in the container where it collects as pure iodine crystals. Vapor from the air is converted directly to the solid (snow) in winter, and is collected on refrigerator pipes as frost.

### PHYSICAL CHANGES

The changes in state just discussed are called physical changes, or physical reactions. The nomenclature is obvious; there was no change in chemical composition. The material lost when heated was recovered when cooled. In freezing water to ice, only the physical aspects of the matter are changed. It is still water. Steam is still water and may be condensed to the common liquid.



## CHEMICAL CHANGES

Water may be changed into the gas phase by a much more energetic and destructive method than described above. If water (containing a little impurity) is electrolyzed, that is, if the opposite poles of a storage battery are connected to platinum strips immersed in the container of water, a gas is bubbled off at each electrode and the quantity of water diminishes.

However, the gas liberated at the platinum strips, the electrodes, is not water vapor. In fact, there are *two* gases, (hydrogen and oxygen) one at each electrode. Liquid water cannot be restored by simply lowering the temperature of the gases and or by increasing the pressure. A chemical change has taken place. In this case another chemical change can restore liquid water. If a mixture of the hydrogen and oxygen gases is ignited, that is, heated to a high temperature locally with a match or spark, oxygen and hydrogen will disappear with an explosion, leaving water vapor, which condenses to water droplets.

Other chemical reactions with which we are acquainted are the burning of gasoline in air to form gases in the automobile engine, the burning of coal to form gases and the hydrogenating of liquid oils in the manufacture of shortening and margarine.

## EXERCISES

1. Name the three physical states of matter.
2. Describe the appearance of each state in terms that distinguish it from each of the other two.
3. Describe the internal structure of the substance in each state.
4. Why is glass not a true solid? Which of the following are true solids: coal tar, ice, paraffin, salt, dry ice, wood?
5. In which state does a substance exhibit the greatest density? The least?
6. Under what conditions does carbon dioxide exist as a liquid?
7. Which may be pure: water, steam or ice? Explain.
8. Define viscosity. Name three substances with high viscosity.
9. How may salt water be separated into pure substances?
10. Which of the following are chemical reactions: the burning of wood, the baking of bread, the drying of sand, the souring of milk, the grinding of salt, the frying of bacon?
11. Which of these processes include a chemical reaction?
  - a. Table salt is heated to 804°C, at which temperature it changes to a colorless liquid. It is cooled to harden suddenly in one translucent piece.
  - b. Blue vitriol (copper sulfate) is heated to 110°C; the blue crystals change to a white powder as water vapor is lost. The white powder is cooled to room temperature in dry air and remains as such.
  - c. Sugar is heated in a crucible to 186°C; it fumes and leaves a black residue.
  - d. Pure oxygen gas is cooled to -183°C; it condenses to a pale blue liquid.
  - e. A piece of ordinary glass is heated until it softens. It is then bent back and forth at that temperature until it becomes cloudy, solidifies and breaks.

THE COMPOSITION  
OF SUBSTANCES

All bodies of matter, either as they appear in nature or as they occur as a result of man's arranging, may be placed in one of two classes. They must be either homogeneous or heterogeneous. A heterogeneous body is an obvious mixture; we can see that it is composed of different materials. Concrete, soil, wood, granite and bean soup are mixtures.

On the other hand, salt water, a gold ring, sugar and air are homogeneous. They are composed of only one phase. A phase constitutes all parts of a system that have exactly the same physical properties. One crystal of sugar has the same properties as any other crystal of sugar, although the sizes may differ. All sugar crystals together constitute a phase. A heterogeneous system contains more than one phase. A mixture of iron and sulfur contains two phases; all particles of iron belong to one phase and all particles of sulfur belong to the other.

The phases of a heterogeneous mixture may be separated in different ways. At times, a solid mixture may be separated into phases with tweezers and a magnifying glass. In a mixture of solid and liquid such as sand in water, one can decant the liquid (pour it off) or filter it. In other cases ingenuity is required. For example, a mixture of sand and salt may be easily separated because they differ greatly in one of their properties: solubility in water. Salt is very soluble while sand is insoluble. To separate them, one need merely to add water, stir and filter. The salt is in the water and the sand on the sieve or filter paper. The salt may be recovered by evaporating the water. Other methods of separation make use of differences in other physical properties, such as melting points, boiling points, etc.

A phase or a homogeneous system may be either a solution or a pure substance. A solution is a homogeneous mixture. Salt water is a solution, a mixture of salt and water. A gold ring, if 14 carat yellow gold, contains 14

parts of gold to 10 parts of copper by weight and is homogeneous. Air is a homogeneous mixture, a gaseous solution.

Pure substances in turn may be separated into two classes, elements and compounds. Elements, by far the smaller group, are combined to make compounds. Compounds are composed of elements. Elements are the substances left when any type of material is reduced to its ultimate chemical

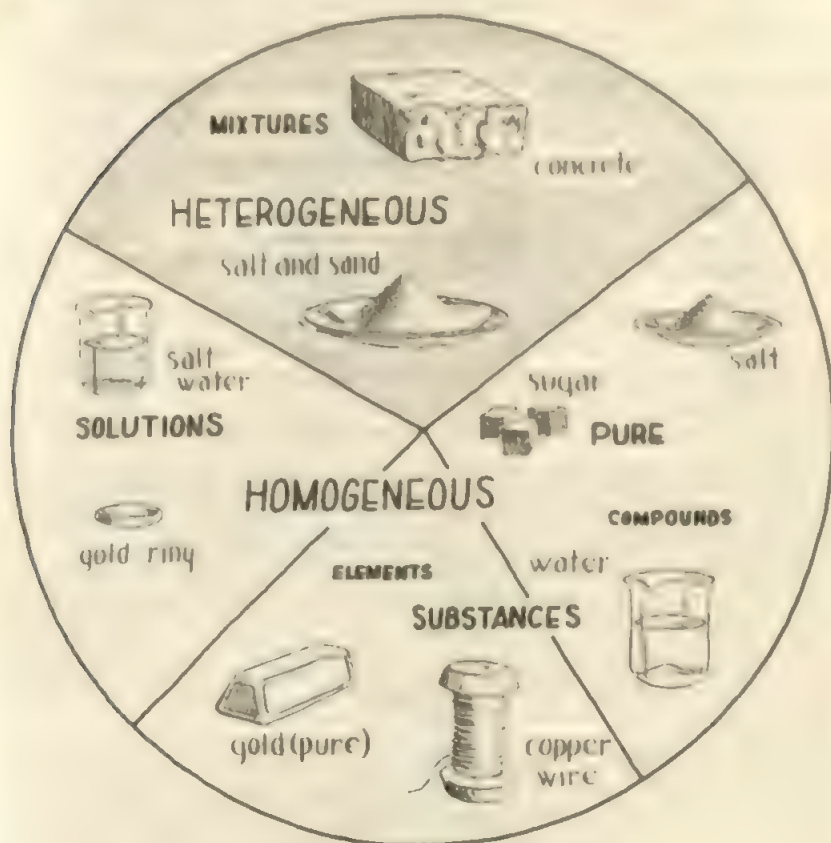


Figure 4.1. Kinds of matter.

constituents. Experimentally it is rather difficult to determine whether a pure substance is a compound or an element. History reveals that many compounds were thought at first to be elements. Substances remain classified as elements only as long as they cannot be shown to be compounds. An element can never be changed to another substance without adding a second substance, nor can it be separated into two or more substances, neither can it be the sole product of the chemical reaction of two or more substances.

There are only about 103 chemical elements known and there is only a

remote possibility that many others will be found. In contrast, there are more than one million different compounds, composed of elements, with the number growing daily as new substances are either isolated or synthesized.

Some of the more common elements are listed with their symbols in Table 4.1.

**Table 4.1. Some of the More Commonly Known Elements**

<i>Element</i>	<i>Symbol</i>	<i>Element</i>	<i>Symbol</i>
Aluminum	Al	Lead	Pb
Arsenic	As	Mercury	Hg
Calcium	Ca	Nickel	Ni
Carbon	C	Nitrogen	N
Chlorine	Cl	Oxygen	O
Copper	Cu	Platinum	Pt
Gold	Au	Silver	Ag
Hydrogen	H	Sodium	Na
Iodine	I	Sulfur	S
Iron	Fe	Uranium	U

The metals (copper, aluminum, iron and gold) are immediately recognizable. Sulfur, a yellow solid, and carbon (charcoal) are commonplace. The nitrogen and oxygen mixture called air is also well-known.

The symbols serve as abbreviations for the elements. They are usually the first one or two letters of the name, with the *first letter in capitals* and the *second letter, if it occurs, a lower case letter*. The symbol is often derived from the Latin name, such as: Ag for silver, from *argentum*, and Na for sodium, from *natrium*. The student should memorize the symbols of the elements listed.

Of the four classes of matter listed, two are more easily characterized: elements and heterogeneous mixtures. Mixtures are apparent, and elements survive vigorous attempts to decompose them. But it is difficult to distinguish between compounds and solutions, because both are homogeneous and both are composed of more than one element. One must look into the nature of their combination to distinguish them. Assistance will be sought in a study of the laws of chemical change.

Scientific laws are statements correlating or summarizing experimental observations. These laws of chemical combination are no exception; their basis is found in the laboratory.

### LAW OF CONSERVATION OF MASS

In a chemical reaction no change can be detected in the total mass of the substances involved, for mass is neither gained nor lost in a chemical reaction.



For example, when 23 g of sodium metal combines with 35.5 g of chlorine gas, 58.5 g of table salt is produced. 58.5 is the sum of 23 g + 35.5 g, and the mass remains constant. This is the case for all reactions studied. The burning of weeds is a chemical reaction. In this process, no mass is lost. If one were to weigh the weeds burned and the oxygen used from the air in the burning, the sum of the two weights would be just equal to the sum of the weights of carbon dioxide and water vapor (that passed off in the air) and the ash left behind. The law of conservation of mass is accepted, because no chemical reaction has yet been observed in which mass was either lost or gained.

The same law applies to physical changes. For example, when salt is dissolved in water, the weight of the salt water is equal to the sum of the weights of the salt and water weighed separately. The Law of Conservation of Mass does not differentiate between compounds and solutions.

### LAW OF DEFINITE PROPORTIONS (CONSTANT COMPOSITION)

This law states that when substances react to form a compound, they do so in a definite ratio by weight. A corollary of this law states that all samples of a given compound contain the same elements in exactly the same weight proportions. When sodium reacts with chlorine gas, 23 grams of sodium reacts with 35.5 grams of chlorine to form table salt. If 24 grams of sodium is allowed to react with 35.5 grams of chlorine, some sodium metal will be left over and one would not dare use it to salt his food. Also, if 23 grams of sodium and 36.5 grams of chlorine were mixed, one gram of deadly chlorine gas would be left over. Sodium chloride is a compound; it has a definite composition regardless of method or place of preparation.

In contrast, the composition of solutions varies within wide limits. Up to 33 grams may be dissolved in 100 grams of water to make salt water. The Law of Definite Proportions distinguishes compounds from solutions.

Another criterion of compound formation becomes apparent if we consider the substances in the above example. Sodium is an active metal that reacts violently with water; chlorine is a greenish, very poisonous gas. The product of their union is sodium chloride, table salt, very different in properties from either. In general, compounds have properties very different from the elements of which they are composed.

An apparent contradiction of the Law of Definite Proportions exists in the fact that when carbon combines with oxygen (burns) the gaseous product may vary from 57 to 73 per cent oxygen by weight, the rest being carbon. The problem is resolved when one realizes that there are two compounds of carbon and oxygen: carbon dioxide and carbon monoxide. Each compound obeys the Law of Definite Proportions, carbon dioxide being 73 per cent oxygen and carbon monoxide 57 per cent. Under differing reaction conditions, one gets varying proportions of the two gases and therefore a varying per cent of oxygen in the mixed gaseous product. Often the same two elements can form two or more compounds, but in each compound the composition is constant.

## THE LAW OF SIMPLE MULTIPLE PROPORTIONS

This law cites a relationship between the relative weights of one element that may combine with another element in a series of compounds. The generalization applies to any series of compounds, each one of which contains both elements. It may be stated as follows: "In a series of compounds containing the same two elements, the weights of one element combined with a set weight of the other element bear a simple ratio to each other."

An example of the application of this law can be made with the three compounds: carbon monoxide, carbon dioxide and carbonic acid. Twenty-eight grams of carbon monoxide contains 12 grams of carbon and 16 grams of oxygen. Forty-four grams of carbon dioxide contains 12 grams of carbon and 32 grams of oxygen. Sixty-two grams of carbonic acid contains 12 grams of carbon, 48 grams of oxygen and 2 grams of hydrogen. Each sample considered contains 12 grams of carbon, but the amounts of oxygen contained with the 12 grams of carbon are 16, 32 and 48 respectively, which are in the ratio of 1 to 2 to 3. The Law of Simple Multiple Proportions is a general law and is obeyed by any series of compounds containing the same two elements.

The Law of Definite Proportions and the Law of Simple Multiple Proportions were the inspiration for Dalton's Atomic Theory. We shall consider the Atomic Theory in the next chapter.

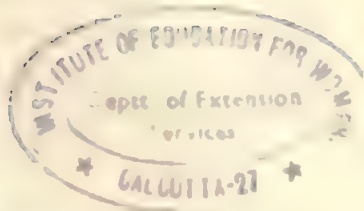
## EXERCISES

1. What two steps of the scientific method are illustrated in this chapter?
2. If the Law of Definite Proportions is ever disproved, how will it be done?
3. In what respect are salt and ice alike, but different from window glass, paraffin and tar?
4. List five homogeneous foods and five heterogeneous foods.
5. List three chemically pure substances, used as such, in human nutrition.
6. 2.00 g of sulfur was burned, consuming 3.00 g of oxygen, to form 5.00 g of sulfur trioxide. Which law of chemical change is demonstrated by this experiment?
7. What elements are contained in the compounds represented by each of these formulas: (a)  $\text{AlPO}_4$ , (b)  $\text{Ca(OH)}_2$ , (c)  $\text{AgNO}_3$ , (d)  $\text{H}_3\text{AsO}_4$ , (e)  $\text{NiCO}_3$ , (f)  $\text{NaCl}$ , (g)  $\text{KIO}_3$ , (h)  $\text{Hg(NO}_3)_2$ , (i)  $\text{Na}_2\text{SO}_4$ , (j)  $\text{Ca(ClO}_3)_2$ ?
8. Which two substances of those listed in Question 7 can be analyzed to illustrate the Law of Simple Multiple Proportions?
9. Samples of five pure substances were analyzed for the same two elements X and Y. The analyses are tabulated below:

Compound	g of X	g of Y
A	2.43	1.42
B	2.43	2.84
C	1.62	1.52
D	1.62	1.42
E	4.86	4.26

Which analysis is incorrect? Why?

10. Define: (a) solution, (b) compound, (c) element, (d) heterogeneous, (e) phase.
11. Which of the following must contain at least two elements: (a) a solution, (b) a compound, (c) a heterogeneous body, (d) a homogeneous body, (e) a pure substance, (f) an impure substance?



## DALTON'S ATOMIC THEORY

At this point our formal knowledge of chemistry is very nearly the same as that of John Dalton, the English Quaker school teacher who at the beginning of the nineteenth century gave voice to the atomic theory of matter. Dalton had personally observed the diffusion of gases into an evacuated space and had observed the interdiffusion of two or more gases to give a homogenous mixture, such as the mixture of nitrogen, oxygen and water vapor we call air. He knew of the combination of elements to form compounds and knew the laws of chemical change discussed in the last chapter. He himself had assisted in formulating the Law of Simple Multiple Proportions. In an attempt to explain these laws and to reconcile his observations of the behavior of gases, he suggested his *Atomic Theory of Matter*. With few amendments it is one of the bases of modern chemistry and has won for its author a place with the greatest chemists of all time.



Dalton's theory may be expressed in these four postulates

1. *All matter is composed of tiny particles (atoms).*
2. *There are several kinds of atoms, differing in both mass and properties. There are as many kinds of atoms as there are elements, and no more, because all atoms of a given element are alike, but differ from those of other elements in both mass and properties.*
3. *Atoms can neither be destroyed, altered nor worn out.*
4. *Atoms may combine to form the smallest units (sometimes molecules) of compounds. Chemical combination is between atoms. They may pair together, make groups of three, etc., but in any case each small unit of a compound is identical to all others, that is, each unit contains the same group of atoms.*


## MOLECULES

According to the atomic theory, a compound must contain identical pairs, identical triplets, or identical cluster of atoms.





FOR EXAMPLE:

if  represents an oxygen atom  
and  a carbon atom,

a carbon monoxide molecule might be 

Any measurable sample of carbon monoxide gas contains diatomic (two-atom) molecules much too small to be seen by any type of microscope. A larger sample of the gas contains more molecules. Carbon dioxide contains molecules of carbon and oxygen, but, as the formula indicates, there are two oxygen atoms with each carbon in the molecule: . Billions of these triatomic (three-atom) molecules are required to make a measurable sample of carbon dioxide gas. Sodium carbonate, washing soda, has a more complicated basic unit. It is composed of sodium, carbon and oxygen.

Two atoms of sodium, one atom of carbon and three atoms of oxygen are joined together.

If  is an oxygen atom,  
 represents a carbon atom,  
and  is a sodium atom,  
 is the sodium carbonate unit.

This picture of molecules is accepted today with amendments to be discussed later in the chapter. Molecule pictures such as those represented above are no longer used. Instead, less cumbersome formulas have replaced them. Elemental symbols are used to designate kinds of atoms. In modern chemical formulas, CO represents a carbon monoxide molecule (one atom of carbon and one atom of oxygen).  $\text{CO}_2$  represents carbon dioxide. The sub-number 2 indicates two oxygen atoms with one carbon atom in the molecule. Likewise, the formula of sodium carbonate,  $\text{Na}_2\text{CO}_3$ , signifies that two sodium, one carbon and three oxygen atoms are contained in a "molecule" of that compound. The formula may indicate the structure (the order and arrangement of the various atoms in the molecule), but very often it does not.

More complicated "molecules" exist in nature. The formula of calcium nitrate is  $\text{Ca}(\text{NO}_3)_2$ . The basic unit of calcium nitrate contains: one calcium atom, two nitrogen atoms, and six oxygen atoms. The sub-number following the parentheses gives the number of the entirely enclosed group of atoms in the unit. The formula  $\text{BaCl}_2 \cdot 2 \text{H}_2\text{O}$  might be written  $\text{BaCl}_2(\text{H}_2\text{O})_2$  and indicates that one barium atom, two chlorine atoms, four hydrogen atoms, and two oxygen atoms form the smallest unit of crystalline barium chloride.

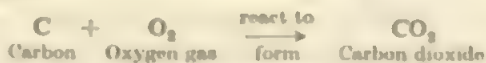
## CHEMICAL EQUATIONS

According to Dalton, a chemical reaction can be a change only in atomic groupings. Since atoms cannot be altered, substances can be changed to



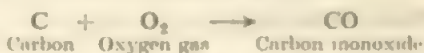
other substances only by rearranging the atoms into new molecules (or groups), by breaking molecules apart, or by both breaking and remaking new molecules.

The burning of coke is a chemical process. Observation has shown the major reaction to be the combining of carbon (coke) with oxygen gas of the air to form carbon dioxide. The reaction is represented by this equation of formulas:

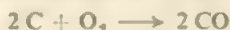


(In oxygen gas, atoms are paired in molecules. This is true of most gases and will be explained later.) The changes in atomic groupings are apparent in the equation. The carbon atom unites with a molecule of oxygen to form a new molecule of carbon dioxide. By convention, carbon and oxygen gas, the substances disappearing, are called reactants and appear to the left of the arrow in the equation; carbon dioxide is the product and appears to the right.

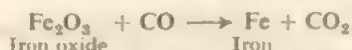
Another reaction occurs when carbon is burned in a limited supply of oxygen. Carbon monoxide is formed:



The symbolical statement is not exactly true since the equation is not balanced. More atoms exist on the left side of the equation than on the right. Since atoms are neither destroyed nor created in a chemical reaction, it is plain that 2 atoms of carbon must react with 1 molecule (of two atoms) of oxygen to yield two molecules (of two atoms) of carbon monoxide. The balanced equation is:



Another and more complicated reaction is that occurring when carbon monoxide gas diffuses into porous iron oxide in the blast furnace. The unbalanced equation for the reaction:



merely shows only the experimental fact that iron oxide and carbon monoxide disappear to leave iron (molten at that temperature) and carbon dioxide. The balanced equation:



shows that 3 molecules of carbon monoxide are required to fully reduce one molecule of iron oxide. Equations must be balanced, that is, the same total numbers and kinds of atoms must appear both in the reactants and the products. This equality must be achieved by placing the correct coefficients (numbers) before the chemical formulas. One determines the correct coefficients by trial and error.

### AGREEMENT OF THEORY WITH LAWS

It becomes apparent that Dalton's Atomic Theory is consistent with the three laws of chemical combination. That is, if his picture is correct, these

laws will be obeyed. The Law of Conservation of Mass will be followed, for atoms are merely regrouped in reaction. Since they cannot be altered, destroyed, nor made in chemical reaction, mass can neither be lost nor gained. Further, if every sub-microscopic molecule of a compound contains an identical group of atoms, all samples of matter containing them will have constant composition, and the elements must combine in *definite proportions*.

Three compounds whose formulas were presented in this chapter contain the same two elements: carbon and oxygen. They are carbon monoxide ( $\text{CO}$ ), carbon dioxide ( $\text{CO}_2$ ) and sodium carbonate ( $\text{Na}_2\text{CO}_3$ ). If amounts of each of these compounds are considered such that each contains the same amount of carbon, the amount of oxygen will be in the ratio of 1 to 2 to 3. If one molecule of each is taken, each has one C atom and the oxygen atoms contained are 1, 2 and 3. Any sample of the materials containing equal molecules will contain an equal weight of carbon and will contain weights of oxygen in the above ratio.

### ATOMIC WEIGHTS

Inherent in Dalton's Atomic Theory is the idea that all atoms, though very small, possess mass. Since the proportion of the elements combined in a compound depends on the masses as well as the number of particles in the formula, it is important to know these masses.

Historically the relative weights of atoms were determined indirectly through an abstract analysis of experimental data involving masses and volumes of gases. We shall consider this method after discussing the gas laws in a later chapter. For the moment we will consider a modern, more direct method by which the atomic weights are found. This method involves the mass spectrograph. We shall consider the principle of operation briefly.

Consider an experiment in which spheres of different densities are dropped from a bridge in the path of a constant, stiff wind. The spheres might be an iron ball, a baseball and a tennis ball. The wind tends to blow the spheres away from the bridge, having little effect on the iron ball, but causing the lighter spheres to fall a considerable distance downwind. The lighter the sphere, the farther it will be carried.

Figure 5.1 is a diagram showing the curved path taken by the respective balls. One could drop several spheres of known densities, marking the spots where they hit the ground. He could then use this scale to find the density of another sphere.

The mass spectrograph uses a similar principle. A gas is bombarded with high speed electrons forming positively charged atoms. These atoms are hurled into a strong electrostatic field and are drawn toward the negative plate. However, the velocity of the particles is such that they cannot turn abruptly, but follow a curved path to strike a photographic plate below. The development of the plate reveals a black line at the point at which the

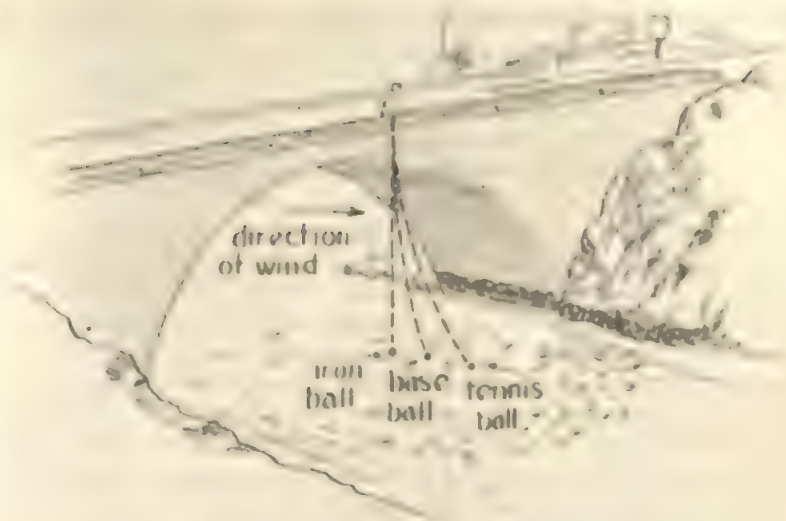


Figure 5.1 Paths of various spheres dropped from a bridge in the wind

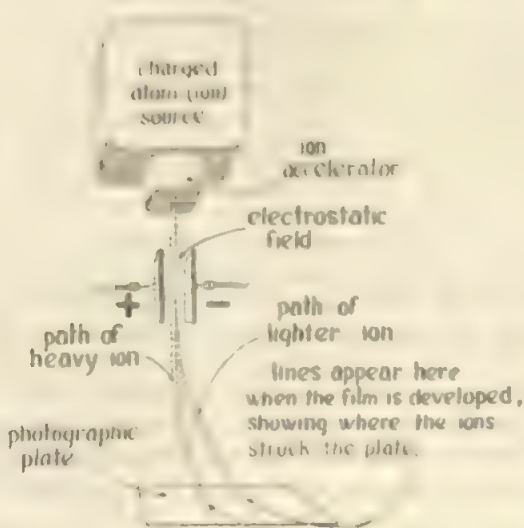


Figure 5.2 Diagram of the mass spectrograph.

charged atoms strike it. Lighter atoms again are pulled farther from the vertical path, while the paths of heavier atoms are bent but little.

Figure 5.2 represents a diagram of the mass spectrograph.

Knowing the charge on the atom, the strength of the electrostatic field, the velocity of the particle and the position where it hits the plate, one can calculate the mass of the atom. Comparison of the positions where hydrogen atoms and oxygen atoms strike the plate shows the oxygen atom to be almost 16

times heavier than the hydrogen atom. More careful examination of the photographic plate shows that not all oxygen atoms are the same, but there are a few of greater mass than the usual atom. Those large atoms have a mass either 1.16 or 1.18 greater than the usual oxygen atom. No atoms have masses in between these values. These three kinds of atoms are called isotopes. Similar experiments have shown that most elements have isotopes, that is, two or more kinds of atoms differing in mass.

Dalton was wrong, it appears, when he postulated that all atoms of an element are identical. Further, it appears that the Law of Definite Proportions is faulty, for a molecule of carbon monoxide with the usual oxygen atom will have a larger percentage of carbon by weight than a molecule containing a carbon atom and a large oxygen atom one-eighth larger than the first. However, this causes no trouble since nature presents us with such a constant mixture of the isotopes. There are  $6 \cdot 10^{16}$  atoms in one cubic millimeter of air (or  $1 \text{ mm}^3$  of  $\text{CO}$ ). One can see the odds against taking a sample of carbon monoxide containing a majority of molecules with the heavy oxygen atom.

Development and refinement of the mass spectrograph, an instrument by which scientists measure the masses of gaseous positive ions, has allowed researchers to set relative values for the atomic mass of each element in relation to the others. To establish a scale of masses one need only set a value for one element and compare all other elements with it. In 1815 Prout saw that if the mass of hydrogen, the smallest atom, were taken as unity, all other atoms would have comparative masses of nearly whole numbers. Consequently, hydrogen was first given a mass of one and the masses of all other atoms were stated in terms equivalent to the number of hydrogens necessary to equal their masses. Later it was found that if the average oxygen atom were said to have a mass of exactly 16.0 the compared masses of most other atoms would be even more nearly integral values. Refinement of techniques in the study of atomic properties soon led to the discovery of isotopes (atoms of the same element which exhibit slightly different mass), and it was noted that the mass of oxygen varied somewhat with different samples and calculation of a suitable average value was difficult. In 1962, by international agreement, this problem was resolved with the adoption of carbon-12, a special isotope of carbon, as the base for comparative values; a value of exactly 12.0 was assigned this element. This gave an easily measured standard to scientists and changed the existing table of values but little. The average oxygen atom shows a mass of 15.9994 compared to carbon-12 as 12.0000.

This number, 15.9994, is called the atomic weight. The atomic weights of some of the more common elements are shown in Table 5.1.

The atomic weight may be defined as the weight of the average atom of an element compared to the carbon-12 atom as 12.0. Observe some of the atomic weights. Notice that an average uranium atom is  $238.03/1.008$  or nearly 238 times as heavy as the average hydrogen atom and is  $238/12$  as heavy as the most common carbon atom.



Table 5.1. Atomic Weight of Some Common Elements

<i>Element</i>	<i>Symbol</i>	<i>Atomic Weight</i>
Aluminum	Al	26.9815
Arsenic	As	74.9216
Calcium	Ca	40.08
Carbon	C	12.01115
Chlorine	Cl	35.453
Copper	Cu	63.54
Gold	Au	196.967
Hydrogen	H	1.00797
Iodine	I	126.9044
Iron	Fe	55.847
Lead	Pb	207.19
Mercury	Hg	200.59
Nickel	Ni	58.71
Nitrogen	N	14.0067
Oxygen	O	15.9994
Platinum	Pt	195.09
Silver	Ag	107.870
Sodium	Na	22.9898
Sulfur	S	32.064
Uranium	U	238.03

### AVOGADRO'S NUMBER AND GRAM-ATOMIC WEIGHTS

As well as determining relative weights of atoms (atomic weights), one can calculate the exact weight of one atom from mass spectrometer data. It is found that the average hydrogen atom weighs  $1.67 \cdot 10^{-24}$  g.

It is useful to know the number of hydrogen atoms in 1.008 g of hydrogen. 1.008 is the atomic weight, and 1.008 g is known as the gram-atomic weight. The number of atoms in it can be found by dividing the weight of an individual atom into the 1.008 g.

$$\frac{1.008 \text{ g-gram-atomic weight}}{1.67 \times 10^{-24} \text{ g/atom}} = 6.02 \cdot 10^{23} \text{ atoms/g-at. wt.}$$

Now the weight of one atom of oxygen is 15.999/1.008 times the weight of a hydrogen atom. Therefore, 15.999 g of oxygen will contain the same number of atoms as 1.008 g of hydrogen, the number again being  $6.02 \times 10^{23}$ . It follows that in every gram atomic weight, there are  $6.02 \times 10^{23}$  atoms. This number is called Avogadro's number and must be remembered. When we study the gas laws, we shall find out how the number obtained its name.

## FORMULA WEIGHTS (MOLECULAR WEIGHTS)

From the table of atomic weights, it can be seen that compared to the carbon-12 atom with a mass of 12.0, the average carbon atom has a mass of 12.0111. It follows that the carbon monoxide molecule, CO, has a mass equal to the sum of the masses of the two atoms,  $12.011 + 15.999 = 28.010$ . The two-atom molecule is 28.010, 12.011 as heavy as the average carbon atom. 28.010 is called the *molecular weight* or the *formula weight* of carbon monoxide. The atomic weight is the relative weight of an atom; the molecular weight is the relative weight of a "molecule." Both weights are relative to the weight of the carbon-12 atom as 12.

The molecular weight of water,  $H_2O$ , is then  $2(1.008) + 15.999 = 18.015$ . The water molecule is about 18/16 as heavy as the oxygen atom. In all cases, reference is made to the average atom and the average molecule.

The molecular weight of sodium sulfate ( $Na_2SO_4$ ) is calculated the same way:

$$\begin{array}{rcl}
 2 \text{ Na} & = & 2 \times 22.990 = 45.980 \\
 1 \text{ S} & = & 32.064 = 32.064 \\
 4 \text{ O} & = & 4 \times 15.999 = 63.996 \\
 & & \hline
 & & 142.040
 \end{array}$$

The molecular or formula weight is 142.040 grams. This is the weight of the seven atom unit relative to the single atom of carbon-12 as 12. The molecular weight is merely the sum of the weights of the atoms present.

It also follows that in 142.040 grams there are  $6.02 \times 10^{23}$  "molecules" (or formula units, each composed of two sodium atoms, one sulfur and four oxygen atoms). In this 142.040 grams there are  $2 \times 6.02 \times 10^{23}$  atoms of sodium,  $6.02 \times 10^{23}$  atoms of sulfur and  $4 \times 6.02 \times 10^{23}$  atoms of oxygen. But since each "molecule" or group contains 2 Na, 1 S and 4 O atoms, there are only  $6.02 \times 10^{23}$  groups. One can say that there are  $6.02 \times 10^{23}$  atoms of an element in one *gram-atomic weight*. Likewise there are  $6.02 \times 10^{23}$  molecules in one *gram-molecular weight*. A better name for gram-molecular weight is *gram-formula weight*. A more common name is *one mole*.

One more example of the calculation of the formula weight or molecular weight might be instructive.

EXAMPLE: Calculate the formula weight of potassium alum,  
 $KAl(SO_4)_2 \cdot 12 H_2O$ .

$$\begin{array}{rcl}
 1 \text{ K} & = & 1 \times 39 = 39 \\
 1 \text{ Al} & = & 1 \times 27 = 27 \\
 2 \text{ S} & = & 2 \times 32 = 64 \\
 8 \text{ O} & = & 8 \times 16 = 128 \\
 24 \text{ H} & = & 24 \times 1 = 24 \\
 12 \text{ O} & = & 12 \times 16 = 192 \\
 & & \hline
 & & 474
 \end{array}$$

Taking integral values of the atomic weights.

The molecular weight of potassium alum is 474. One of these 48 atom units weighs 474/12 as much as one carbon-12 atom. Furthermore, in one mole, 474 g, of potassium alum there are  $6.02 \times 10^{23}$  of these 48 atom units.

## CALCULATION OF ELEMENTAL COMPOSITION

If one knows the formula of a compound, he can use the atomic weights to calculate the weight of each element in a sample of the compound.

**EXAMPLE:** How many grams of oxygen are there in 50 g of water?

$$2 \text{ H} = 2 \times 1 = 2 \text{ parts H}$$

$$1 \text{ O} = 1 \times 16 = 16 \text{ parts O}$$

in 18 total parts

16/18 of any amount of water is oxygen

$$16/18 \times 50 \text{ g} = 44.5 \text{ g of oxygen in 50 g of water}$$

$$2/18 \times 50 \text{ g} = 5.5 \text{ g of hydrogen in 50 g of water}$$

$$\text{and } 44.5 \text{ g} + 5.5 \text{ g} = 50 \text{ g total}$$

**EXAMPLE:** How many grams of potassium are there in 68 g of  $\text{KClO}_3$ ?  
Adding the atomic weights as found in the Periodic Table

$$\text{K} = 39$$

$$\text{Cl} = 35.5$$

$$3 \text{ O} = 48$$

$$\hline 122.5$$

$$39/122.5 \times 68 \text{ g} = 21.6 \text{ g K in 68 g KClO}_3.$$

## CALCULATION OF PERCENTAGE COMPOSITION

This is similar to the above calculation. One merely takes the fraction of 100%.

**EXAMPLE:** What is the percentage composition of water?

$$\text{Again } 2 \text{ H} = 2 \times 1 = 2$$

$$\text{O} = 1 \times 16 = 16$$

$$\hline 18$$

$$2/18 \times 100\% = 11\% \text{ hydrogen}$$

$$16/18 \times 100\% = 89\% \text{ oxygen}$$

$$\hline 100\% \text{ total}$$

**EXAMPLE:** Calculate the percentage composition of potassium chlorate,  $\text{KClO}_3$ ?

$$\text{K} = 39$$

$$\text{Cl} = 35.5$$

$$3 \text{ O} = 48$$

$$\hline 122.5$$

$$\frac{39}{122.5} \times 100\% = 31.8\% \text{ K}$$

$$\frac{35.5}{122.5} \times 100\% = 29.0\% \text{ Cl}$$

$$\frac{48}{122.5} \times 100\% = 39.2\% \text{ O}$$

$$\hline 100.0\% \text{ Total}$$

## SIMPLEST FORMULA

The simplest ratio of atoms in a molecule (gram-atomic weights in 1 mole) of a compound can be found from an analysis of that compound if one uses the atomic weights. These ratios give us the formula. The formula  $\text{CO}_2$  tells two facts: There are one C and two O atoms per molecule, and the ratio of the number of atomic weights of carbon to the number of atomic weights of oxygen in the compound is 1 to 2. Likewise sodium, sulfur and oxygen are combined in sodium sulfate,  $\text{Na}_2\text{SO}_4$ , in the ratio of 2 gram-atomic weights to 1 gram-atomic weight to 4 gram-atomic weights respectively. When one finds that ratio, he has the simplest formula. The examples below illustrate the method.

**EXAMPLE 1.** A 100 g sample of a compound of hydrogen and oxygen contains 11.1 g of hydrogen and 88.9 g of oxygen. Calculate the simplest formula.

There are 11.1 g of hydrogen to 88.9 g of oxygen. For each gram-atomic weight of oxygen (16 g), there are

$$\frac{16 \text{ g}}{88.9 \text{ g}} \times 11.1 \text{ g} = 2 \text{ g of hydrogen}$$

Two g of hydrogen is

$$\frac{2 \text{ g}}{1 \text{ g/gram-at. wt.}} = 2 \text{ gram at. wts.}$$

The simplest formula is



**EXAMPLE 2.** A sample of an iron oxide contains 0.252 g of iron and 0.096 g of oxygen. Find the simplest formula consistent with this data.

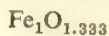
With 56 g of iron (1 gram-atomic weight) there would be

$$\frac{56 \text{ g}}{0.252 \text{ g}} \times 0.096 \text{ g} = 21.4 \text{ g of oxygen}$$

or

$$\frac{21.4 \text{ g}}{16 \text{ g/gram-at. wt.}} = 1.333 \text{ gram-at. wt. of oxygen}$$

The ratio of gram-atomic weights is shown by the formula:



Multiplying the gram-atomic weight ratios by 3 gives the smallest whole number ratio



In summary the following may be noted:

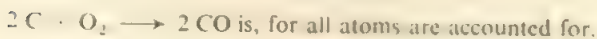
1. The Atomic Theory was a product of the scientific method. Quantitative observations were summarized into the laws of chemical combination. Dalton formulated the theory to explain those laws. The theory has been examined and amended.



2. There are two notable amendments to the theory :
  - a. All atoms of an element are not identical, but an element is usually a constant mixture of two or three kinds of atoms of nearly the same mass.
  - b. Atoms can be destroyed. Some like radium decompose spontaneously; others only after being bombarded with high energy particles. However, these are not chemical reactions, and do not occur with the chemicals and conditions one normally uses in the laboratory.
3. Chemical reactions are merely regrouping of atoms. The equation of the reaction denotes equality in number and kinds of atoms in the reactants and in the products. The equation must be a balanced equation.



but



### EXERCISES: SET I

Balance each of the following equations:

1.  $\text{CaO} + \text{HCl} \longrightarrow \text{CaCl}_2 + \text{H}_2\text{O}$
2.  $\text{H}_2\text{SO}_4 + \text{NaOH} \longrightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$
3.  $\text{Fe} + \text{H}_2\text{O} \xrightarrow{\Delta} \text{Fe}_3\text{O}_4 + \text{H}_2$
4.  $\text{Mg} + \text{N}_2 \xrightarrow{\Delta} \text{Mg}_3\text{N}_2$
5.  $\text{H}_2\text{O} + \text{Na} \longrightarrow \text{H}_2 + \text{NaOH}$
6.  $\text{C} + \text{H}_2\text{O} \xrightarrow{\Delta} \text{CO} + \text{H}_2$
7.  $\text{C}_3\text{H}_8 + \text{O}_2 \longrightarrow \text{CO}_2 + \text{H}_2\text{O}$
8.  $\text{C}_3\text{H}_8 + \text{H}_2\text{O} \longrightarrow \text{CO}_2 + \text{H}_2$
9.  $\text{Al}_2(\text{SO}_4)_3 + \text{H}_2\text{O} \longrightarrow \text{Al}(\text{OH})_3 + \text{H}_2\text{SO}_4$
10.  $\text{PCl}_5 + \text{H}_2\text{O} \longrightarrow \text{H}_3\text{PO}_4 + \text{HCl}$
11.  $\text{Cl}_2 + \text{H}_2\text{O} \longrightarrow \text{HCl} + \text{O}_2$
12.  $\text{H}_3\text{S}_2\text{O}_7 + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_4$
13.  $\text{H}_2\text{O}_2 + \text{N}_2\text{H}_4 \cdot \text{H}_2\text{O} \longrightarrow \text{N}_2 + \text{H}_2\text{O}$
14.  $\text{PbS} + \text{H}_2\text{O}_2 \longrightarrow \text{PbSO}_4 + \text{H}_2\text{O}$
15.  $\text{Ag}_2\text{O} + \text{H}_2\text{O}_2 \longrightarrow \text{Ag} + \text{H}_2\text{O} + \text{O}_2$
16.  $\text{Fe}_2\text{O}_3 + \text{H}_2 \longrightarrow \text{Fe} + \text{H}_2\text{O}$
17.  $\text{Fe}_2\text{O}_3 + \text{C} \longrightarrow \text{Fe} + \text{CO}_2$

### EXERCISES: Set II

1. Write, to hand in, and know the symbols for the elements: gold, silver, mercury, barium, tin, lead, iodine, bromine, iron and nickel.
2. The atomic weight of sodium is 22.997, of iron is 55.85, of oxygen is 16.000 and of hydrogen is 1.008.
  - a. Which contains more atoms, 1 gram of hydrogen or 10 grams of oxygen?

- b. Will 55.85 pounds of iron have the same number of atoms as 1.008 pounds of hydrogen?
- c. Which of the elements listed above has atoms of the greatest mass?
- d. What is the molecular weight of  $\text{Fe}_2\text{O}_3$ ?
- e. How many pounds of  $\text{Fe}_2\text{O}_3$  have the same number of molecules as there are atoms in 8 pounds of oxygen?
3. a. How many sulfur atoms are there in 1 molecule of  $\text{Al}_2(\text{SO}_4)_3$  (aluminum sulfate)?
- b. How many oxygen atoms are there in 1 molecule of  $\text{Al}_2(\text{SO}_4)_3$ ?
- c. How many atoms are there in 1 molecule of  $\text{Al}_2(\text{SO}_4)_3$ ?
4. a. How many sulfur atoms are there in 1 "mole" (1 gram-molecular weight) of  $\text{Al}_2(\text{SO}_4)_3$ ?
- b. How many oxygen atoms are there in 1 mole of  $\text{Al}_2(\text{SO}_4)_3$ ?
- c. How many atoms are there in 1 mole of  $\text{Al}_2(\text{SO}_4)_3$ ?

### PROBLEMS

Atomic Weights: Na = 23; Cl = 35.5; S = 32; Ca = 40; N = 14; C = 12; Al = 27; H = 1.0; Ba = 137.

1. Calculate the molecular weight of:
  - a. NaCl
  - b.  $\text{SO}_3$
  - c.  $\text{Ca}(\text{NO}_3)_2$
  - d.  $\text{Na}_2\text{CO}_3$
  - e.  $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$
  - f.  $\text{BaCl}_2 \cdot 2 \text{H}_2\text{O}$
  - g.  $\text{Ba}(\text{OH})_2$
  - h.  $\text{CCl}_4$
2. What fraction of the mass of
  - a.  $\text{NaCl}$  is chlorine
  - b.  $\text{SO}_3$  is oxygen
  - c.  $\text{Na}_2\text{CO}_3$  is sodium
  - d.  $\text{Ca}(\text{NO}_3)_2$  is oxygen
  - e.  $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$  is oxygen
3. How many grams of oxygen are there in:
  - a. 60 g of  $\text{SO}_3$
  - b. 60 g of  $\text{SO}_2$
  - c. 75 g of  $\text{CaSO}_4$
  - d. 80 g of  $\text{Ba}(\text{OH})_2$
  - e. 160 g of  $\text{Al}_2(\text{SO}_4)_3$
4. What is the per cent of
  - a. oxygen in  $\text{SO}_3$
  - b. sulfur in  $\text{SO}_2$
  - c. sodium in  $\text{Na}_2\text{SO}_4$
  - d. sulfur in  $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$
  - e. sodium in  $\text{NaClO}_3$
5. Calculate the percentage composition of
  - a.  $\text{Na}_2\text{CO}_3$
  - b.  $\text{CaSO}_3$
  - c.  $\text{BaCl}_2 \cdot 2 \text{H}_2\text{O}$
6. Calculate the simplest formula for each of the compounds described below.
  - a. 50 g of a compound of sodium, phosphorus, and oxygen contains 21.04 g Na and 9.45 g P.
  - b. The oxide which constitutes the most important source of manganese contains 63.19% manganese.
  - c. An oxide of manganese in which manganese and oxygen are combined in the ratio by weight of 1.717 to 1.000.
  - d. 74.91 g of arsenic (As) is combined with 3.024 g of hydrogen in arsine.
  - e. In the oxide, white arsenic, 74.91 g of As is combined with 24.00 g oxygen.
  - f. A 25 g sample of a compound contains 7.97 g K, 7.23 g Cl and 9.79 g O.
  - g. 50 g of a compound contains 13.29 g K, 17.68 g Cr and 19.04 g O.
7. A compound of hydrogen and nitrogen contains the two elements in the ratio of 3 to 21 g. Calculate the simplest formula. The molecular weight of the compound is 32. What is the molecular formula?
8. Show that the compounds:  $\text{NO}_2$ ,  $\text{NO}$  and  $\text{N}_2\text{O}$  obey the Law of Simple Multiple Proportions.  
*Show your method in all calculations.*
9. a. How many atoms are there in one formula of  $\text{Ca}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ ?
- b. Calculate the molecular weight of  $\text{Ca}(\text{NO}_3)_2$ .
10. How many grams of calcium are there in 25 g of calcium carbonate ( $\text{CaCO}_3$ )?
11. Calculate the mass of 16 ml of concentrated hydrochloric acid. Density is 1.37 g/ml.

# CHAPTER 6

## ATOMIC STRUCTURE

According to the Atomic Theory, compounds are composed of identical "clusters" or groups of atoms. Different compounds differ in the number, kinds and arrangement of the atoms in the cluster. Each cluster may be simply a pair of two unlike atoms or a group of three or four or more up to a thousand.

Simple or complex, it is important to know the nature of the forces that hold the atoms together. A knowledge of the compositions of the individual atoms themselves assists in this understanding. Despite the submicroscopic size of the atoms, much is known of the still smaller particles of which they are constructed. We shall discuss these briefly.

### SUB-ATOMIC PARTICLES, THE "BUILDING BLOCKS" OF ATOMS

#### ELECTRON

The most familiar atomic fragment is the electron. The electron is the carrier of electricity. A stream of electrons moving along a metallic conductor constitutes an electric current. We can observe some properties of these electrons if we force them to jump across a void. This is done in a *cathode ray tube*.

A cathode ray tube (Fig. 6.1) is a cylindrical vacuum tube with an electrode (a metal disk) at each end. The electrode is connected to a wire sealed through the glass wall of the tube. In operation a high voltage is placed across the cell, charging one electrode (the cathode) negatively and the other electrode (the anode) positively. A small but measurable current flows through the vacuum. Furthermore, at the anode, ( + ) end of the tube, the glass tubing beyond the

anode glows faintly except where the shadow of the electrode is cast. The glowing of the tube is said to be caused by invisible *cathode rays* that emanate from the cathode toward the anode. Those that miss the anode target and strike the glass cause it to glow. The operation of this tube suggests that the rays are negative particles: negative, because they leave the cathode (—) and are drawn toward the anode (+); and particles (that is, they possess mass), because they have inertia and do not bend abruptly when passing the anode, but continue on a short distance to strike the glass.



Figure 6.1. Cathode ray tube.

A clearer picture of the electron can be obtained by a modified cathode ray tube (Fig. 6.2). In this tube a large disk is placed in front of the cathode. The disk has a slit across the middle and serves to stop all the rays except those passing through the slit. A thin metal strip treated so that impacts of cathode rays cause it to glow is placed diagonally across the tube from the end of the slit described above to the opposite end of the tube.

When the high voltage is impressed across the tube as before, a straight, green-glowing line traces the image of the slit on the screen (Fig. 6.2b) showing the particles to be traveling in a straight line after being hurled through the slit. Now when an electric field is placed about the screen with the positive pole above and the negative pole below, the green line is seen to curve upward beginning at the slit in the anode (Fig. 6.2c). Again the rays bend toward the positive pole, (are negatively charged) and again the curve is gradual showing that the momentum of the particles (the “mass in motion”) resists the bending force.

The picture tube of a television set is a modified cathode ray tube. An electron gun (cathode) fires electrons toward the front of the tube. Electron impacts on the treated inner surface of the front face of the tube cause it to glow, lighting up the tube. The glowing is seen on the outside of the tube, the television screen. By an automatic changing of the electrostatic field around the electron stream within the tube, the electrons are made to spray across the front of the tube in strips, similar to the way words are written



across the page of a letter. The electrons spray across the tube so rapidly that the face is covered in a fraction of a second and the whole picture glows. Any dark portion of the picture being "shot" stops the spray of the electrons, leaving that part of the strip dark. Thus we obtain a black and white picture.

The magnitude of the charge of the electron was determined by the Nobel Prize-winning experiment by Dr. Robert A. Millikan (about 1910), in which an oil drop of known mass surrounding a particle of 1 electron charge was



Figure 6.2. Cathode rays.

held suspended in an electrostatic field. The experiment will not be discussed here, but the results will be used. The electron charge is  $1.6 \times 10^{-19}$  coulomb.

A current of approximately 1 ampere flows through a lighted 100-watt bulb.

An ampere is 1 coulomb per second or  $\frac{1}{1.6 \times 10^{-19}} = 6.3 \times 10^{18} = (6,300,000,000,000,000,000,000,000)$  electrons per second. Knowing the charge, one can calculate the mass of an electron from the extent of its bending in an electrostatic field as above (Mass Spectrograph principle). Compared to an oxygen atom as 16, and a hydrogen atom as 1.008, the electron has a mass of  $1/1837$  and is very light, even compared to an atom.

We are interested primarily in the electron not as a carrier of electricity, but as a part of an atom. This knowledge came first from a study of radioactivity. Radium decomposes into other elements with the emission of three types of rays: alpha, beta and gamma rays. When these rays are studied in an electrostatic field, alpha rays bend slightly toward the negative pole; beta rays curve more sharply toward the positive pole; gamma rays are unaffected.

The beta ray has been shown to be an electron hurled from a radioactive atom. The alpha ray is a particle much heavier than an electron, having a mass of approximately 4 units when compared to the carbon atom as 12. Its

charge is positive and is exactly twice that of the electron. The alpha particle is not considered a building block of atoms, for it in turn appears to be composed of still smaller particles which will be discussed presently. Upon gaining two electrons, the alpha particle becomes a helium gas atom.

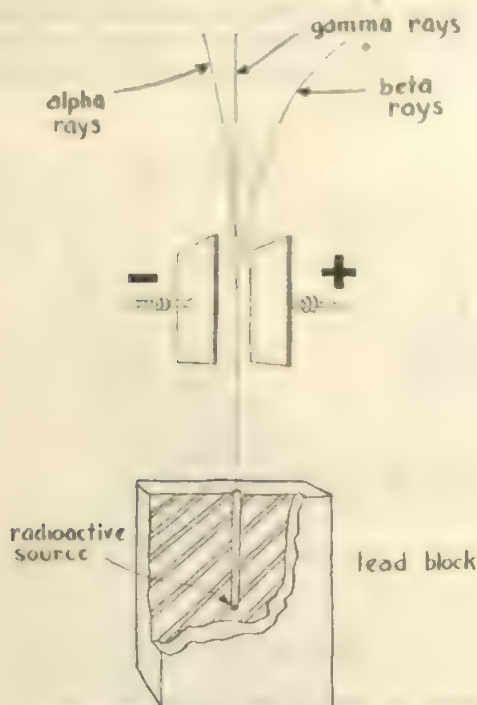


Figure 6.3. Alpha, beta and gamma rays from radium.

The gamma ray is a high energy light radiation. It is similar to an X-ray, but contains more energy. The X-ray will penetrate flesh, but not bones, and therefore will show the bones on a photographic plate activated by the X-rays that pass through a portion of the human body. Gamma rays pass through the bones as well. Both destroy body tissue and both have been used to destroy cancerous cells; at the same time they destroy normal cells. In any case, since gamma rays are light-like radiations, they are not fundamental particles of matter.

### POSITIVE PARTICLES

When a gas is admitted to the cathode-ray tube in low pressure, and the voltage impressed, a bright glow is observed. The color of the light emitted is characteristic of the gas in the tube. If the gas is neon, the light is bright red; if sodium vapor, intense yellow; if mercury vapor, a light green. You have seen these three types as neon signs, sodium vapor street light, and as ultra-violet lights. The common fluorescent light contains a mixture of gases. The

inner surface of the tube is coated with a phosphorescent material. The gas inside and the coating are called *cathode rays*.

If the negative end of the tube is perforated (Fig. 6.4), the glow can be seen in the tube a short distance beyond it. This indicates that there are positive particles in the tube which are drawn toward the negative electrode. When they are largely freed, they pass on through, hence the light beyond the cathode.

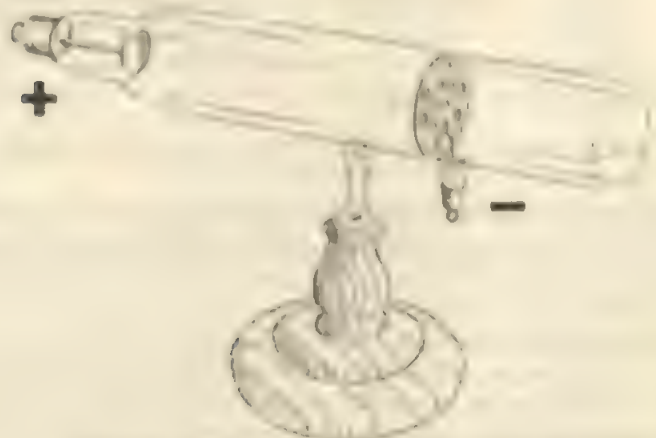
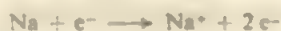


Figure 6.4. Fluorescent tube with perforated cathode

Further investigation has shown these positive particles to have a mass very nearly the same as the atoms of the gas in the tube; they are the atoms minus an electron or two. The electrons liberated from the cathode and accelerated toward the anode strike the molecules of the gas with sufficient force to dislodge an electron, leaving a positive particle. For a sodium atom in vapor, the reaction is:

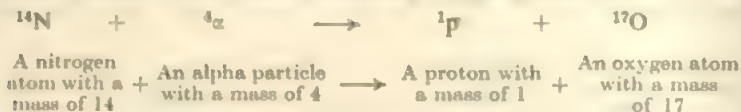


The positive sodium atom now called an ion moves toward the cathode (—) and the electrons continue on toward the anode. When the sodium ion gains another electron from around the cathode it emits the characteristic light.

#### PROTON

When it is bombarded with electrons, hydrogen gas gives the smallest positive particles of all gases since the hydrogen atom is the smallest. This particle, a hydrogen ion, or  $\text{H}^+$  is also called by another name, *proton*, and is represented by  $p^+$ . Note here that electrons are removed from atoms with relatively small energy, and their removal does not permanently change the atom losing them. Upon capturing another electron, the atom is restored. We shall consider this fact later.

The proton is singled out because it can be produced by more energetic means from substances other than hydrogen. When alpha particles from decomposing radium are hurled at high velocity into nitrogen gas, particles having the same charge and mass as a proton are ejected. Further these particles become hydrogen gas on gaining electrons. At the same time, oxygen gas is created. The reaction occurring is represented below.

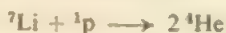


Another process yielding protons is represented below:



Aluminum is permanently changed to silicon by accepting an alpha particle and losing a proton.

Protons may also be absorbed into an atom and thus change it into an atom of another element. For example, a proton hurled into a lithium atom changes it to 2 helium atoms.



Many other reactions in which a proton is either absorbed or expelled by an atom are known. In each case the atom is changed into another kind. On the basis of these reactions, it has gained recognition as a fundamental building unit of the atom. In summary, the proton has a mass of approximately 1 compared to the carbon atom as 12, and has a charge equal in magnitude to the electron, but of opposite sign.

### NEUTRON

Another type of radiation is observed when alpha particles bombard targets of certain light metals such as beryllium and lithium. At first this radiation was classed as short wave, very energetic gamma rays, for they were not deflected in an electric field, but were more penetrating than any gamma rays known. Further experiment showed that the radiation would dislodge protons from paraffin wax. Paraffin contains hydrogen as one of its elements, but a gamma ray devoid of mass would be unable to dislodge it. It was concluded from the velocity of the ejected proton that the radiation was composed of neutral particles with a mass somewhat near that of the proton. A study of the product of the original bombardment verified this, as shown by the equation:



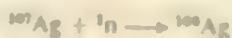
The sum of the mass units of beryllium and the alpha particle is 13; the carbon atom formed from their union is 12. The mass of the particle should be about 1. This is the case. It was named a neutron, a contraction of neutral-proton. In summary, the third building block is the neutron, which has no charge and a mass of about 1 compared to the hydrogen atom.



Two other reactions are cited: the conversion of an oxygen atom and a proton to a fluorine atom and a neutron



and the conversion of the common silver atom to a heavier isotope by absorption of a neutron,

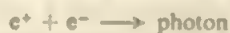


Much more evidence could be cited for the neutron, but this is perhaps enough to justify its position as an atomic structural unit. The neutron holds an important position in world affairs. It is the particle responsible for the propagation of the chain reaction occurring in an exploding atomic bomb.

### OTHER PARTICLES OF MATTER

Thus far, four particles of matter have been discussed. Three of these, the electron, proton, and neutron, are very important as building blocks of matter. The fourth, the alpha particle, is not so important, for it appears to be an intermediate structural unit, being made up itself of two neutrons and two protons. Three of the other elementary particles of matter known are mentioned.

The bombarding of magnesium or aluminum with alpha particles releases, among other particles, one having a mass equal to an electron and a charge equal to that of an electron, but of opposite sign. This particle, called the *positron*, eluded discovery for some time because of its attraction for the ever present electron. On collision the positron and electron are destroyed to give rise to a photon, a quantity of light, by the following equation:



Cosmic ray investigations revealed the existence of another particle, the *meson*, which has an electrical charge equal to that of an electron, but either positive or negative, and a mass about one-tenth that of the proton.

Finally comes the *neutrino*, an electrically neutral particle of mass equal to or less than that of the electron. Mathematical calculations indicate that such a particle exists so that momentum and mass are conserved. Other fragments are known, but are not of sufficient importance for our study.

### RELATIVE NUMBER OF PARTICLES IN THE ATOM

In the preceding section, the sub-atomic particles of matter were presented along with some experimental evidence of their existence and properties. These are summarized below, the mass of the particles being compared to the chemist's atomic weight scale. Three of the particles will be considered further, namely, the neutron, the proton and the electron. These three particles placed together in various numbers, combinations and arrangements are necessary and sufficient to explain the structure of all the lighter atoms. Discussion of more complex atoms will be reserved for further studies.

An atom may be defined as an electrically neutral particle composed of electrons, protons and neutrons, with only one center, which exists as an entity for sufficient time for its properties to be studied.

The number of particles in an atom varies from one atomic species to another. The number and kind of particles in an atom determine its properties. All atoms having the same number of protons are so nearly identical

Name	Symbol	Mass	Charge
H atom	H	1.00797	0
Carbon-12 isotope	$^{12}\text{C}$	12	0
Electron	$e^-$	1/1837	-1
Proton	$p^+$	1.0072	+1
Neutron	$n$	1.0086	0
Positron	$e^+$	1/1837	+1
Meson		ca. 1/10	$\pm 1$
Neutrino		very small	0

chemically that they are classed together, known by that number and are given the same name. For example, all atoms containing only 1 proton are hydrogen atoms and have an atomic number of 1. All oxygen atoms (atomic number 8) contain 8 protons. Elements are listed in the periodic table by increasing atomic number (proton number). Part of the table is reproduced below.

Memorize these elements with the corresponding atomic number. It is well to learn them as they stand in the table in the rows of 8.

The number of electrons in the atom is also given by the atomic number, because the atom must contain an equal number of negative and positive particles to be neutral. Chlorine has an atomic number of 17 and possesses 17 protons and 17 electrons.

There is no exact relationship between the atomic number and the number of neutrons in an atom. One can calculate the number of neutrons if he knows both the atomic number and the weight of the atom. For example, consider the major isotope of aluminum with atomic number 13 and mass 27, represented as  $^{27}_{13}\text{Al}$ . The atom contains 13  $p^+$ , accounting for 13 mass units.

1								2
H								He
3	4	5	6	7	8	9	10	
Li	Be	B	C	N	O	F	Ne	
11	12	13	14	15	16	17	18	
Na	Mg	Al	Si	P	S	Cl	Ar	
19	20	21						
K	Ca	Sc						

It also contains 13  $e^-$  but their mass is negligible. The balance of the mass must be accounted for by neutrons.

$$27 - 13 = 14$$

Each neutron has a mass of approximately 1, so there are 14 neutrons.

The number of neutrons may always be found by subtracting the atomic number from the mass number. Another example: uranium has an atomic number of 92 and an atomic weight of 238.07 ( $^{238}_{92}\text{U}$ ).

$$\begin{array}{l} 92 e^- \\ 92 p^+ \\ \text{and } 238 - 92 = 146 n \end{array}$$

Application of this method shows that, among lighter elements, the atom contains nearly an equal number of neutrons and electrons. As the atomic number increases, the ratio of neutrons to protons increases up to about 3 to 2 among the heaviest atoms. One of the heaviest, uranium, has a ratio 146/92, more than 3 to 2.

Isotopes were defined previously as atoms of the same element with different masses. Since they are atoms of the same element, isotopes contain the same number of protons and electrons. The difference in mass must be due to a different number of neutrons in the two atoms. Compare the two isotopes of chlorine, one with a mass of 35, the other with a mass of 37.

$$\begin{array}{ll} {}^{35}_{17}\text{Cl} & 17 p^+ \\ & 17 e^- \\ & 35 - 17 = 18 n \end{array} \qquad \begin{array}{ll} {}^{37}_{17}\text{Cl} & 17 p^+ \\ & 17 e^- \\ & 37 - 17 = 20 n \end{array}$$

## REGIONS WITHIN THE ATOM

In 1911 Ernest Rutherford devised and carried out a simple experiment that gave chemists some idea of atomic structure. When an alpha particle strikes a metal surface coated with ZnS, a bright flash occurs. If one turns a sample of radium imbedded in a lead block toward a piece of metal coated with zinc sulfide, a spot in the center is seen to glow brightly (Fig. 6.5a).

Rutherford placed a thin piece of gold foil between the alpha-emitting radium and the zinc sulfide screen (Fig. 6.5b). The gold foil was very thin—4000 Å, or 0.00004 cm, thick. However, there were 1000 layers of atoms in the foil. He could see no difference in the intensity of the light at the center of the zinc sulfide screen. Apparently the alpha particles went right through. Occasionally, however, an isolated flash or scintillation appeared on the side of the screen. Then the screen was moved to other positions around and facing the metal foil, occasional scintillations were observed at any angle. Some alpha particles bounced directly back. Further studies showed that only 1 in 100,000 alpha particles deviated from the straight line. Those that did might appear at any angle from the foil.

Rutherford reasoned that since most alpha particles went straight through the foil, they could have hit none of the particles except possibly an electron with its negligible mass. Therefore, an atom is mostly vacant space. If only 1 in 100,000 particles were deflected by 1000 rows of atoms, only 1 in 100,000,000

would be deflected by one layer of gold atoms. He reasoned further that the total mass of the atom must be in one small unit, the center of the atom, the *nucleus*, because when the alpha particle did hit something, it was heavy enough to bounce the particle off in any direction. This would mean that all the protons and all the neutrons must be in a tiny nucleus, whereas the electrons with their negligible mass might take up the space about the nucleus.

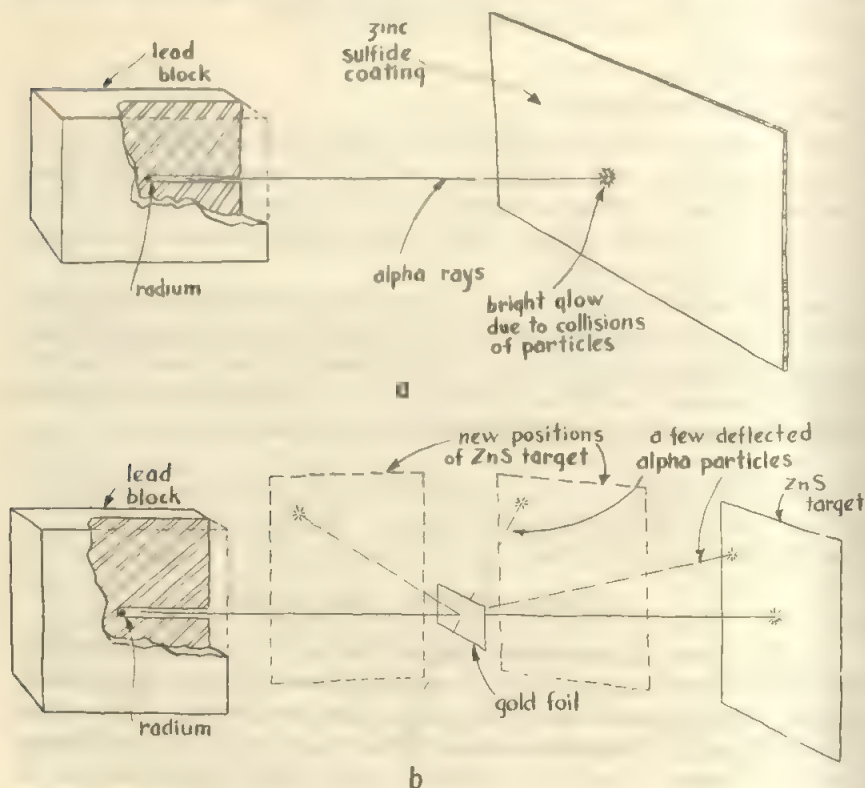


Figure 6.5a. Alpha particles striking a ZnS covered screen.

b. Alpha particles passing through a gold foil.

He thought of the atom as a tiny solar system, with the nucleus corresponding to the sun and the electrons rotating around the nucleus as the planets do about the sun. The nucleus with its circling electrons was like a spinning top keeping all other matter away.

Using the figures from above and other experimental results, we find that the nucleus has about  $1/10,000$  the diameter of the whole atom. The nucleus has a diameter about  $10^{-12}$  cm; the atom diameter is approximately  $10^{-8}$  cm. These diameters vary from atom to atom, but are of this order.

This picture of the neutrons and protons bound tightly in a small nucleus with the electrons about it agrees with the energies required to remove the particles from the atom. Electrons are rather easily removed by electron impact in a cathode ray tube. Removal of either protons or neutrons requires



collision with a high energy alpha particle or other high energy particles. Further, the ion (atom minus an electron) soon finds another electron and reverts to its former self. Loss of a proton or neutron permanently changes the atom.

One can now understand why the ratio of neutrons to protons in an atom increases from 1 to 1 in light elements, up to 3 to 2 for heavier elements. Protons repel one another because of their like electrostatic charge. On the other hand there is a "gravity-like" attraction between them. These gravity-like forces are insufficient to hold them together in the nucleus unless almost an equal number of neutrons with their gravity-like attraction and no electrostatic repulsive forces are present. As more protons are crowded into the tiny nucleus, more and more neutrons must be added to hold them together. Finally, the nucleus becomes so large that it is unstable.

### ELECTRONIC STRUCTURE

For our purposes, nothing more need be said about the nucleus, or the neutrons and protons of which it is composed. These particles have little to do with the chemical activity of the atom. The electron arrangement about the nucleus is important, since it holds the key to the bonding characteristics of an atom. It shall be considered here.

First, one should note that the electron is held in its position about the nucleus by the electrostatic attraction between it and the positively charged nucleus. The questions follow, "Why doesn't the electron fall into the nucleus?" "What keeps it out in the tremendous space surrounding the small, charged center?" The answer is found in the fact that atoms contain energy. The energy is explained by a simple atomic model as the kinetic energy of the electron as it circles the nucleus in its orbit.

There is evidence that an atom can exist in any one of a number of energy states; that is, that an electron (or electrons) can occupy any one of a number of orbits, depending upon the energy it possesses. This is the case for a hydrogen atom, the simplest of all, which has only one electron about its proton nucleus. As an analogy, consider the swinging of an object on the end of a string in a circle (Fig. 6.6).

With no motion, no energy, the object hangs straight down. However, as energy in the form of circular motion is given to it, it swings out and up against gravity. In Figure 6.6a the weight has little kinetic energy. In Figure 6.6b the weight is moving much faster, has more energy and describes a wider arc. The greater the energy, the greater the diameter of the circle as the object surges out and up.

According to Rutherford's model, the electron swings out in a "wider" orbit as more energy is given to it. Here the analogy ends. In contrast to the weight on the string which may change gradually from a small to a larger circular path, the electron must jump from one to the other. There are certain defined orbits and the electron must receive exactly the right amount of

energy to lift it from one to another. The hydrogen atom may be represented as in Figure 6.7.

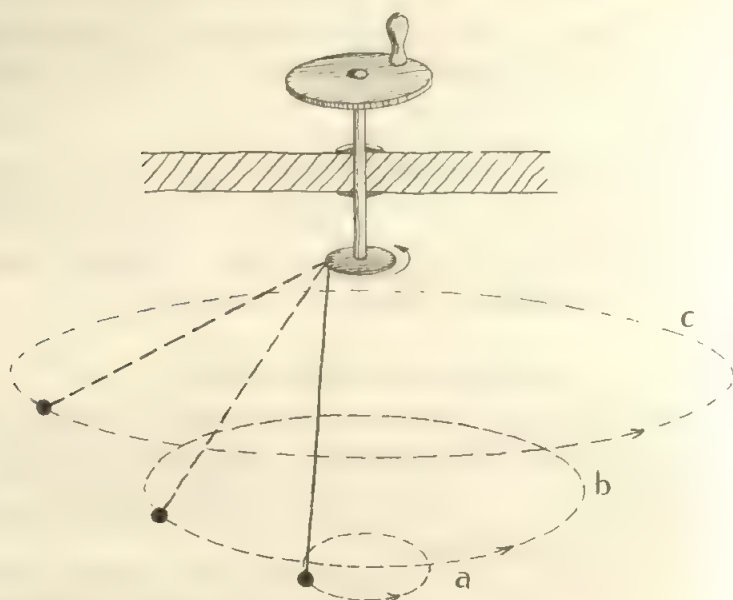


Figure 6.6. Object at end of a string.

About the nucleus there are many orbits. In this sketch the electron is placed in the innermost orbit, and the atom is said to be in the ground state. By absorption of energy, the electron may be lifted into one of the higher orbits.

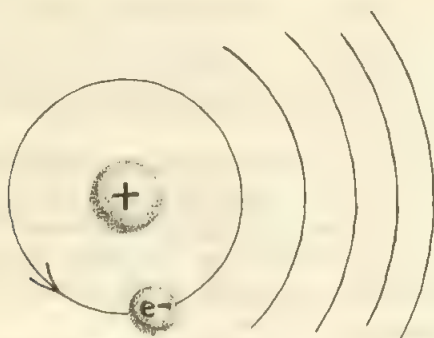


Figure 6.7. Hydrogen atom.

### SPECTRA: EVIDENCE FOR ORBITS

Experimental evidence for the electron orbit theory discussed above comes from a more careful examination of the light emitted from fluorescent lamps.

It was mentioned before that sodium gives a yellow light, mercury a green light and neon a bright red light when the gases are bombarded by cathode rays in a partial vacuum. The color of the light is characteristic of the gas in the fluorescent tube. Hydrogen gas fluoresces with a light blue color. By passing the light from a hydrogen lamp through a prism it can be separated

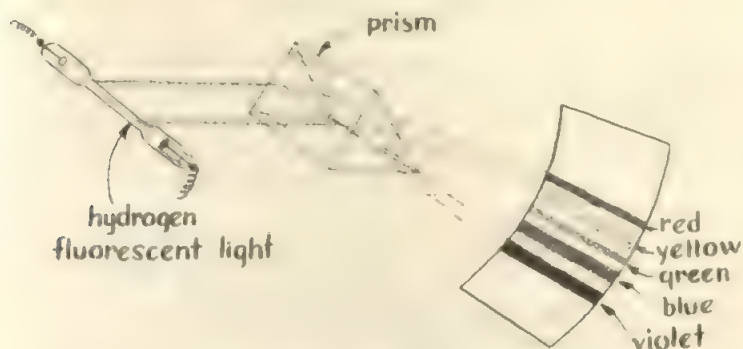


Figure 6.8. Hydrogen spectrum.

into color components. When this is done, all colors are not visible, but certain colors are (Fig. 6.8).

When the light is cast on photographic film after passing through the prism and the film is developed, lines appear where the narrow band of color appeared.

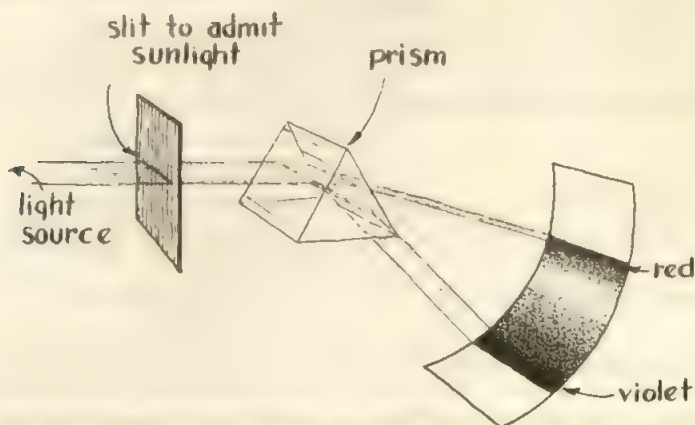


Figure 6.9. Spectrum of sunlight.

This picture may be contrasted with the color make-up or spectrum of sunlight. When sunlight is passed through a prism, it gives the complete rainbow (Fig. 6.9). There is no break between colors; all colors are there. It is known that the energy of the photons, which are packages of radiant energy,

varies with the color of the photon. Red photons have the smallest energy, yellow have more, followed by green, blue and finally violet, which contains the largest energy photons of visible light. Separating the light colors by a prism also separates the photons according to the energy they possess.

Sunlight contains light of all energies. Light green fluorescing hydrogen contains only certain definite size energy packages. The hydrogen model with electron orbits (Fig. 6.10a) is used to explain this. When cathode rays strike

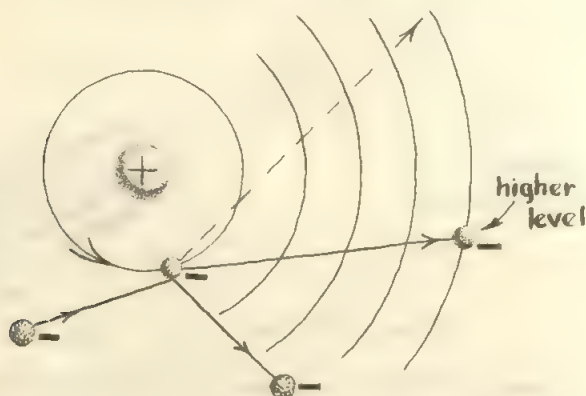


Figure 6.10a. Diagram of electron levels in hydrogen.

the electron of a hydrogen atom, the electron may be completely removed from the atom, leaving the ion, which then migrates toward the cathode. Or, as shown in Figure 6.10a, the electron may receive just enough energy to lift it to a higher energy orbit within the atom.

The colliding particle is slowed down by the collision, some of its energy being taken up in raising the electron to a higher level. The electron tends to return to the lowest orbit possible, the ground state. It may do so in one step

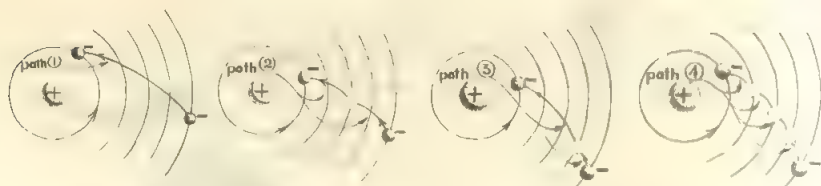


Figure 6.10b. Paths by which an electron may return to the lowest level.

or in many steps, as shown in Paths 1, 2, 3 and 4 in Figure 6.10b, but only by giving up energy as photons of light.

Path 1 would probably yield a violet, high energy photon; both steps in 2 might yield green, and each step in 4 might yield a red photon. The total energy yielded in all four steps of 4 must equal the energy yielded in the one step in 1, etc.

In a hydrogen lamp there are billions and billions of atoms "excited" every



instant by the impact of electrons; each electron may return by one of the paths shown or by other paths. In any case there will be great numbers jumping from level 4 to 3; 4 to 2; 4 to 1; 3 to 1, etc. For each of these there is a definite size photon. These correspond to definite energies and to thin definite lines on the photographic film when the spectrum of hydrogen is taken.

### ORBITAL ARRANGEMENT

Rutherford's original picture of the atom has undergone many changes. Now it is admitted that the electron might possibly have energy between energy levels; but the probability is almost negligible. The electrons are no longer thought to follow only circular and elliptical orbits; they are found in certain geometrical volumes called orbitals.

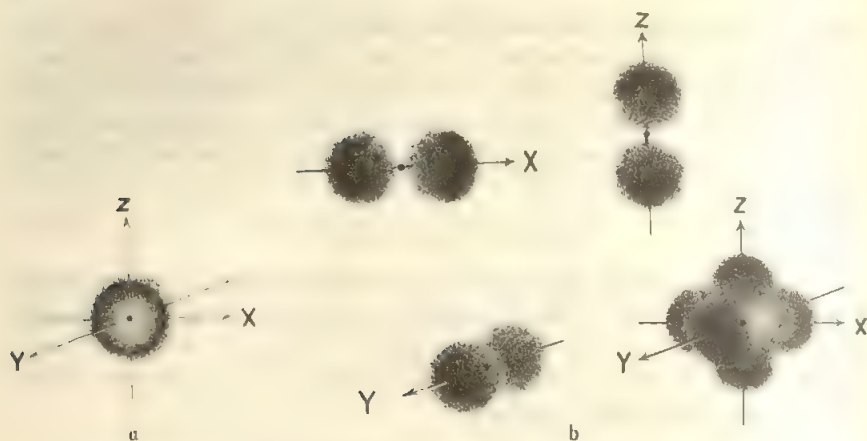
**Table 6.1. Number of Orbitals in Each Quantum Level**

<i>Level Number, <math>n</math></i>	<i>Number of Orbitals, <math>n^2</math></i>
1	1
2	4
3	9
4	16
5	25
6	36

The orbital arrangement of an atom is not so simple as shown in Table 6.1. Each atom has many possible orbitals in which electrons might be found. Orbitals may differ both in their shapes and in the energy possessed by an electron in them. Fortunately, the orbital arrangement is similar in all atoms, whether the orbitals are occupied or unoccupied. That is, the hydrogen atom has the same orbitals as a uranium atom, although in hydrogen only one orbital, usually the one of lowest energy, contains an electron.

To aid in mathematical studies of spectra, orbitals are classified or divided into quantum levels (shells), numbered consecutively from 1. The number of orbitals within a quantum level increases with the level number, according to the formula  $n^2$ , where  $n$  is the level number. Table 6.1 lists the number of orbitals in each quantum level. As the quantum number ( $n$ ) increases, the energy of an electron in the level increases.

The orbitals within a given quantum level are not all alike. They may differ in both shape and energy. Orbitals of equal energy within a quantum level have the same shape and constitute a sublevel. The number of sub-levels



First sub-level

The three orbitals of the second sub-level

Figure 6.11a and b. Some atomic orbitals.

within the various quantum levels and the number of orbitals per sub-level are tabulated in Table 6.2. Quantum level 1 has one sub-level; quantum level 2, two; quantum level 3, three, etc. The number of orbitals "all identical" per sub-level increases from 1 to 3 to 5 to 7, etc., in every quantum level (until the maximum for that level). The lowest energy orbital of each quantum level (which constitutes the first sub-level of that quantum level) is a sphere. That is, the volume where the electron occupying that orbital is most likely to be found may be circumscribed by a sphere about the nucleus as the center (Fig. 6.11a). That orbital is called an s-orbital. Obviously, there is only one possible spherical orbital, with the same radius and the same center; hence there is only one orbital in the first sub-level of each quantum level. The s-orbital of each succeeding quantum level has a greater radius (Fig. 6.11c).

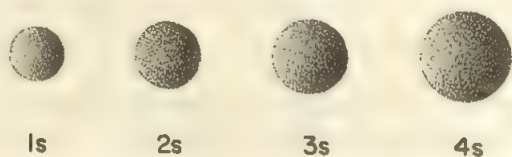


Figure 6.11c. Comparative size of the first sub-shell orbitals of quantum levels 1 to 4.

Orbitals of the second sub-shell of quantum levels 2, 3, 4, 5, etc. (quantum level number 1 has only one sub-level) are three in number. They are in the shape of two spheres touching at the nucleus. The three orbitals, called p-orbitals, of one sub-level are shown separately as  $p_x$ ,  $p_y$  and  $p_z$  and then together in Figure 6.11b. An electron occupying one of these orbitals is most likely to be found (has the greatest probability) at one of two points on opposite sides and equidistant from the nucleus. The probability fades in all directions from each of these points making the touching spheres. One can see that the 3 p-orbitals are identical in shape. However, they differ in orientation. With their axes mutually perpendicular, a set of three unique



Figure 6.11d. Comparative volumes of second sub-shell orbitals of quantum levels 2 to 4.

orbitals of the same shape and volume can exist. p-Orbitals of succeeding quantum levels circumscribe an increasing volume, as represented in Figure 6.11d.

Each of the five orbitals of the third sub-level of each quantum level beginning with quantum level number 3 are shaped like four spheres in a plane grouped about the nucleus like the four leaves of a four-leafed clover (Fig. 6.11e). There are five of these orbitals called d-orbitals. The orientation of these orbitals with respect to one another will not be discussed here. Each of the orbitals of the 4th subshell have "8 probability lobes" and are very complicated; a drawing will not be attempted. They are named f-orbitals.

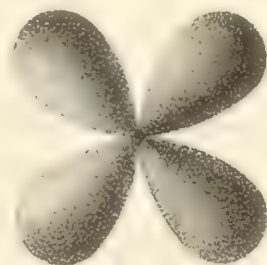


Figure 6.11e. Shape of an orbital of the 3rd sub-shell.

Relative energies of the orbitals in the sub-levels are represented in Figure 6.12; each succeeding quantum level contains orbitals of higher energy. Some

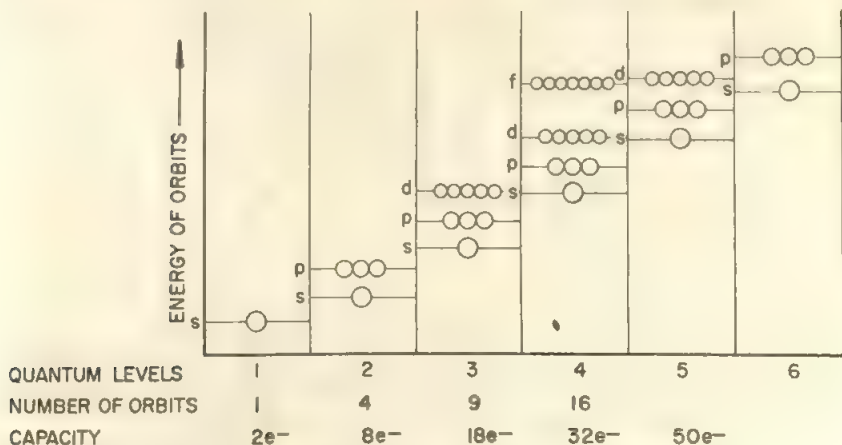


Figure 6.12. Relative energies of electrons in sub-levels.

**Table 6.2. Electron Capacities of Quantum Levels and Sub-levels**

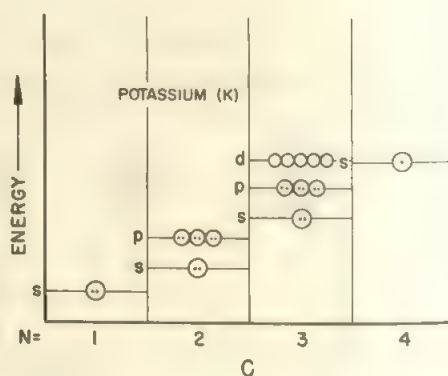
Quantum Level $n$	Orbitals per Sub-level	Electrons per Sub-level	Quantum Level Capacity $2n^2$
5	9	18	50
	7	14	
	5	10	
	3	6	
	1	2	
4	7	14	32
	5	10	
	3	6	
	1	2	
3	5	10	18
	3	6	
	1	2	
2	3	6	8
	1	2	
1	1	2	2

LEVELS	SUB-LEVELS
8	6
8	2
2	2

A

LEVELS	SUB-LEVELS
2	1
8	6
8	2
8	6
1	2

B

**Figure 6.13. Electronic configurations of argon and potassium.**

levels overlap so that the lowest sub-group of a level may contain an orbital of lower energy than those of the highest sub-group of the preceding quantum level. These relative energies are determined from atomic spectra.

Each orbital may contain one or two electrons. The electron capacities of the sub-levels and quantum levels are shown in Table 6.2.





Table 6.4. Electron Configuration of the Atoms

Element	Atomic No.	1	2	3	4	5	6	7
H	1	1						
He	2	2						
Li	3	2	1					
Be	4	2	2					
B	5	2	3					
C	6	2	4					
N	7	2	5					
O	8	2	6					
F	9	2	7					
Ne	10	2	8					
Na	11	2	8	1				
Mg	12	2	8	2				
Al	13	2	8	3				
Si	14	2	8	4				
P	15	2	8	5				
S	16	2	8	6				
Cl	17	2	8	7				
Ar	18	2	8	8				
K	19	2	8	8	1			
Ca	20	2	8	8	2			
Sc	21	2	8	9	2			
Ti	22	2	8	10	2			
V	23	2	8	11	2			
Cr	24	2	8	13	1			
Mn	25	2	8	13	2			
Fe	26	2	8	14	2			
Co	27	2	8	15	2			
Ni	28	2	8	16	2			
Cu	29	2	8	18	1			
Zn	30	2	8	18	2			
Ga	31	2	8	18	3			
Ge	32	2	8	18	4			
As	33	2	8	18	5			
Se	34	2	8	18	6			
Br	35	2	8	18	7			
Kr	36	2	8	18	8			
Rb	37	2	8	18	8	1		
Sr	38	2	8	18	8	2		
Y	39	2	8	18	9	2		
Zr	40	2	8	18	10	2		
Nb	41	2	8	18	12	1		
Mo	42	2	8	18	13	1		
Tc	43	2	8	18	14	1		
Ru	44	2	8	18	15	1		
Rh	45	2	8	18	16	1		
Pd	46	2	8	18	18			
Ag	47	2	8	18	18	1		
Cd	48	2	8	18	18	2		

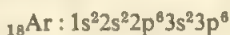
Table 6.4. Electron Configuration of the Atoms (Cont'd.)

Element	Atomic No.	1	2	3	4	5	6	7
In	49	2	8	18	18	3		
Sn	50	2	8	18	18	4		
Sb	51	2	8	18	18	5		
Te	52	2	8	18	18	6		
I	53	2	8	18	18	7		
Xe	54	2	8	18	18	8		
Cs	55	2	8	18	18	8	1	
Ba	56	2	8	18	18	8	2	
La	57	2	8	18	18	9	2	
Ce	58	2	8	18	20	8	2	
Pr	59	2	8	18	21	8	2	
Nd	60	2	8	18	22	8	2	
Pm	61	2	8	18	23	8	2	
Sm	62	2	8	18	24	8	2	
Eu	63	2	8	18	25	8	2	
Gd	64	2	8	18	25	9	2	
Tb	65	2	8	18	26	9	2	
Dy	66	2	8	18	27	9	2	
Ho	67	2	8	18	28	9	2	
Er	68	2	8	18	29	9	2	
Tu	69	2	8	18	31	8	2	
Yb	70	2	8	18	32	8	2	
Lu	71	2	8	18	32	9	2	
Hf	72	2	8	18	32	10	2	
Ta	73	2	8	18	32	11	2	
W	74	2	8	18	32	12	2	
Re	75	2	8	18	32	13	2	
Os	76	2	8	18	32	14	2	
Ir	77	2	8	18	32	15	2	
Pt	78	2	8	18	32	17	1	
Au	79	2	8	18	32	18	1	
Hg	80	2	8	18	32	18	2	
Tl	81	2	8	18	32	18	3	
Pb	82	2	8	18	32	18	4	
Bi	83	2	8	18	32	18	5	
Po	84	2	8	18	32	18	6	
At	85	2	8	18	32	18	7	
Rn	86	2	8	18	32	18	8	
Fr	87	2	8	18	32	18	8	1
Ra	88	2	8	18	32	18	8	2
Ac	89	2	8	18	32	18	9	2
*Th	90	2	8	18	32	19	9	2
*Pa	91	2	8	18	32	20	9	2
*U	92	2	8	18	32	21	9	2
*Np	93	2	8	18	32	22	9	2
*Pu	94	2	8	18	32	23	9	2
*Am	95	2	8	18	32	24	9	2
*Cm	96	2	8	18	32	25	9	2
*Bk	97	2	8	18	32	26	9	2
*Cf	98	2	8	18	32	27	9	2
*Es	99	2	8	18	32	28	9	2
*Fm	100	2	8	18	32	29	9	2
*Md	101	2	8	18	32	30	9	2
*No	102	2	8	18	32	31	9	2
*Lw	103	2	8	18	32	32	9	2

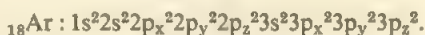
\* Probable configurations

The electron configurations of the atoms in the ground or usual state can now be determined. The student should remember that electrons occupy the lowest energy orbitals possible. That is, the lowest energy orbitals are filled first. Table 6.3 is constructed following this principle.

The electronic configuration of argon is represented in the table in Figure 6.13a by level and sub-level, beginning with quantum level 1 at the bottom. The 18 electrons are distributed: 2 in quantum level 1; 8 in quantum level 2 (2 in the 1 orbital of sub-level 1 and 6 in the 3 orbitals of sub-level 2); and 8 in quantum level 3 (in sub-levels as in quantum level 3). The electron structure of argon (in sub-levels) is written as:



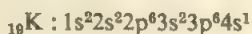
in individual orbitals as:



The meaning of the symbols is as represented below.

$1s^2$	2 electrons in the s or first sub-level of quantum level number 1
$3p_x^2$	2 electrons in the $p_x$ orbital (one of the second sub-level orbitals) of the third quantum level

The electron structure of the potassium atom is as represented in Figure 6.13 B and C. The structure in symbolic notation is:

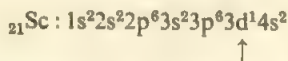


(The total number of electrons in the atom is the sum of the super-script numbers.)

In the potassium atom, the first quantum level is filled with 2 electrons ( $1s^2$ ), the second quantum level is filled to capacity with 8 ( $2s^2 2p^6$ ), but the third quantum level contains only 8 electrons ( $3s^2 3p^6$ ) of a total capacity of 18 represented by ( $3s^2 3p^6 3d^{10}$ ). Nevertheless, the 19th electron of potassium enters the 4s sub-level, leaving 5 orbitals of the third quantum level vacant. This occurs because electrons fill the orbitals in the order of increasing energy. The 4s orbital has a lower energy than the 3d orbitals and is filled first. Calcium, with 20 electrons, has the following electron structure:



Scandium (atomic number 21) has this electron configuration:



With the 4s orbital filled the five 3d orbitals are next in energy. The nine succeeding elements,  ${}_{22}\text{Ti}$  to  ${}_{30}\text{Zn}$ , contain from 2 to 10 electrons in the 3d sub-level. The series of elements from scandium to zinc in which the "under" quantum level is filled with from 9 to 18 electrons is called transition elements.



## EXERCISES

1. What carries the electric current through a cathode ray tube?
2. What experimental evidence is there that cathode rays are not light rays?
3. What are gamma rays?
4. Describe the kinds of rays emitted by radium.
5. What happens to the alpha particle lost by radium?
6. Describe the principle of operation of the picture tube in a television set.
7. What is an ion?
8. What evidence is there that positive ions are present in a fluorescent tube?
9. How is the mass of the proton determined?
10. What evidence is there that the proton is a fundamental unit of all atoms?
11. Why should a neutron ray be more penetrating (approach closer to the nuclei of atoms) than rays of either alpha particles or protons?
12. What is the composition of the alpha particle in terms of protons and neutrons?
13. Give the reasoning behind the conclusion Rutherford made from the results of his alpha particle—gold foil experiment.
14. What other supporting evidence is there that electrons are outside the nucleus and therefore more loosely bound than protons and neutrons?
15. Give the compositions of the following atoms in protons, neutrons and electrons:  
(a)  $^{16}_8\text{O}$  (b)  $^{35}_{17}\text{Cl}$  (c)  $^{37}_{17}\text{Cl}$  (d) the common isotope of calcium, (e) the common isotope of bismuth.
16. Write the notation for the most abundant isotope of each element below as is done here for the most abundant isotope of oxygen:  $^{16}_8\text{O}$ .  
(a) helium, (b) sodium, (c) cesium, (d) potassium, (e) vanadium, (f) uranium, (g) radon.
17. Give two definitions of isotopes.
18. Write the capacities of the first 5 electron energy levels of an atom.
19. List the visible light colors in the order of increasing energy of the photons.
20. Define an orbit. How many electrons may occupy a single orbit at one time?
21. Define the term transition element.
22. Why is the neutron to proton ratio greater in larger atoms than in the first 20?
23. Why are there never more than 8 electrons in the outermost quantum level?
24. Why should scandium and calcium be more alike chemically than potassium and calcium?
25. What similarity in electron structure exists among the following atoms: oxygen, sulfur, tellurium and selenium?
26. Write an electron configuration for a magnesium atom that might momentarily emit a photon.
27. Why does the 19th electron of potassium enter the fourth quantum level when the third is incomplete?
28. Radium, with a mass of 226, emits an alpha particle. Show the atomic species formed using this type of notation:  $^{226}_{88}\text{Ra}$ .
29. Where does the alpha particle ejected from the radium nucleus gain the necessary electrons to become a helium gas atom?
30. A radium atom,  $^{226}_{88}\text{Ra}$ , may decay to  $^{206}_{82}\text{Pb}$  by the stepwise emission of these particles in this order: alpha, alpha, alpha, beta, beta, alpha, beta, beta and alpha. Indicate all atomic species that occur in the decay sequence by the type notation used for radium and lead.
31. Write the electron sub-shell configuration for the following atoms: Fe, O, Br, Mg, N, S, F and Sc. Example:  $^{17}_{17}\text{Cl}: 1s^2 2s^2 2p^6 3s^2 3p^5$

## CHEMICAL BONDING

## 1. PERIODIC TABLE

In the last chapter, the first 21 elements of the Periodic Table were considered in the order and position they occupy in the table. They were seen to be listed according to increasing atomic number in rows of 2, 8, 8 and 18, one below the other, such that elements with the same number of electrons in the outermost level fall in the same vertical column.

Lest one assume that a knowledge of electronic structure enabled chemists to arrange the elements in a systematic table, it should be noted that electrons were not known until over 30 years after the table was in use. At that time the only picture of atomic structure was the one proposed by Prout, who believed that all atomic weights are integral multiples of the atomic weight of hydrogen. He said, therefore, all other atoms are composed of an integral number of hydrogen atoms. Even this mistaken idea of structure had little to do with the development of the table. It grew from studies of the chemical properties of the elements.

In 1829 Döbereiner suggested that like elements occurred in groups of three, which he called "triads." He further noted that within these groups the elements had either very nearly the same atomic weight or that the atomic weight of one element is midway between those of the other two. The atomic weights of the triad, iron, cobalt, and nickel, are very nearly the same. On the other hand lithium, sodium and potassium; calcium, strontium and barium; and chlorine, bromine and iodine are similar groups in which the middle element has an atomic weight midway between the other two.

In 1852 Dumas observed that like elements differ in atomic weight by some multiple of 8. For example consider the atomic weights of lithium (7), sodium (23) and potassium (39). They differ by steps of 16 units.

Thirteen years later, Newlands saw a further relationship between atomic weights and chemical properties. He noted that when the elements are listed in the order of increasing atomic weights, they fall in groups of seven, each group repeating one by one, the properties of the first seven. Not considering hydrogen and helium, he listed them as below (Table 7.1).

**Table 7.1. Newlands' Octaves**

Li	Be	B	C	N	O	F
Na	Mg	Al	Si	P	S	Cl
K	Ca	Cr	Ti	Mn	Fe	Co and Ni

By comparison with the Periodic Table, one can see that the atomic weights increase through each row, reading left to right. The properties are repeated; that is, sodium and potassium have properties similar to those of lithium, etc., until chromium (Cr), titanium (Ti) and the other transition elements appear. The inert gases are not found in his arrangement for they were not known. His successive groups of seven elements with the eighth repeating properties of the first were likened to the musical scale, and were called "Newlands' Octaves".

Newlands had taken a great step toward constructing the Periodic Table, but it remained for Dimitri Mendeleev and Lothar Meyer, working independently of each other, to develop the table much as we have it now. Both published their papers in 1869. The two tables are quite similar. Meyer's table is shown on the next page.

Like Newlands, he left hydrogen and helium out. The transition elements he placed in a row by themselves, mismatching them with elements of the main groups. His table is remarkable when one realizes that he knew perhaps only 57 of the 103 elements we know today. Compare his table with the large periodic table included in this chapter (Table 7.3).

Changes of the table since that time have been mainly additions. However, in some few cases, where the atomic weights do not follow the atomic numbers, elements have been exchanged. In the modern table, elements are arranged in rows in the order of increasing atomic number. The rows are of such length that similar elements fall in the same vertical column or groups.

## 2. THE NON-BONDERS—NOBLE GASES

An interesting paradox exists in the fact that an understanding of the nature of chemical bonding can be aided by studying the particular elements that form few chemical bonds. These are the so-called noble gases, the elements appearing in the last group of the Periodic Table (Table 7.4).

Table 7.2. Lothar Meyer's Periodic Table

I	II	III	IV	V	VI	VII	VIII	IX
	B 11.0	Al 27.3				?In 113.4		Tl 202.7
	C 11.97	Si 28				Sn 117.8		Pb 207.4
			Ti 48		Zr 89.7			
	N 14.01	P 30.9		As 74.9		Sb 122.1		Bi 207.5
			V 51.2		Nb 93.7		Ta 182.2	
	O 15.96	S 31.98		Se 78		Te 128?		
			Cr 52.4		Mo 95.6		W 183.5	
	F 19.1	Cl 35.38		Br 79.75		I 126.5		
			Mn 54.8		Ru 103.5		Os 198.6	
			Fe 55.9		Rh 104.1		Ir 196.7	
			Co=Ni 58.6		Pd 106.2		Pt 196.7	
Li 7.01	Na 22.99	K 39.04		Rb 85.2		Cs 132.7		
			Cu 63.3		Ag 107.66		Au 196.2	
?Be 9.3	Mg 23.9	Ca 39.9		Sr 87.0		Ba 136.8		
			Zn 64.9		Cd 111.6		Hg 199.8	



### Table 7.3. Periodic Table

Group Numbers																																														
Period	1a	2a	3b	4b	5b	6b	7b	8b	1b	2b	3a	4a	5a	6a	7a	0																														
I 2 Elements	H 1															He 2																														
II 8 Elements	Li 3	Be 4									B 5	C 6	N 7	O 8	F 9	Ne 10																														
III 8 Elements	Na 11	Mg 12									Al 13	Si 14	P 15	S 16	Cl 17	Ar 18																														
IV 18 Elements	K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34																														
V 18 Elements	Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52																														
VI 32 Elements	Cs 55	Ba 56	La and 57 58-71	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84																														
VII	Fr 87	Ra 88	Ac and 89 90-102												At 85	Rn 86																														
<table><tr><td>Lanthanides</td><td>Ce 58</td><td>Pr 59</td><td>Nd 60</td><td>Pm 61</td><td>Sm 62</td><td>Eu 63</td><td>Gd 64</td><td>Tb 65</td><td>Dy 66</td><td>Ho 67</td><td>Er 68</td><td>Tm 69</td><td>Yb 70</td><td>Lu 71</td></tr><tr><td>Actinides</td><td>Th 90</td><td>Pa 91</td><td>U 92</td><td>Np 93</td><td>Pu 94</td><td>Am 95</td><td>Cm 96</td><td>Bk 97</td><td>Cf 98</td><td>Es 99</td><td>Fm 100</td><td>Md 101</td><td>No 102</td><td>Lw 103</td></tr></table>																	Lanthanides	Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71	Actinides	Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102	Lw 103
Lanthanides	Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71																																
Actinides	Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102	Lw 103																																

Table 7.4. The Inert Gases in the Periodic Table

H																			He
Li	Be												B	C	N	O	F		Ne
Na	Mg												Al	Si	P	S	Cl		Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br			Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I			Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At			Rn
		Lu																	
Fr	Ra	Ac																	
		Lw																	

These elements are "new" elements. It has previously been noted that they were not known nor even suspected when the periodic table was first constructed. Argon, helium, krypton and xenon were identified in the last 10 years of the nineteenth century. Radon was discovered during the next 10-year period.

Argon was the first identified. In 1785, Cavendish mixed oxygen with air and passed a spark through it repeatedly until no further reaction took place. The reaction is the same one occurring in air with lightning:

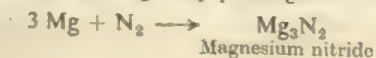


Nitrogen of the air combined both with oxygen of the air and the oxygen added to give nitrogen dioxide. The nitrogen dioxide was then dissolved in potassium hydroxide solution by bubbling the gas through the solution. Excess oxygen was removed by properly passing the rest of the gas over hot copper.



When he did this, Cavendish reported that a little gas remained, amounting to about 1/120th of the volume of his original sample of air. Apparently he never guessed that he had isolated a new element.

In 1894, Lord Rayleigh prepared nitrogen gas by two different methods: by removing oxygen and carbon dioxide from dry air, and by decomposing ammonia,  $\text{NH}_3$ . He found that nitrogen from air had a density of 1.2572 g/L while that from ammonia had a density of 1.2506. Rayleigh knew he had not made an error as large as the difference between the two. He reasoned correctly that the atmosphere must contain an unknown elemental gas of density greater than nitrogen. With Sir William Ramsay, he investigated large quantities of air, removing the oxygen by passing the gas over hot copper, and removing the nitrogen by passing it over hot magnesium.



Again, as in Cavendish's experiments, a small residue of gas remained. The gas was identified spectroscopically and named argon (inert). It is interesting that Cavendish's 1/120th part agrees well with the 0.9% argon in air.

Helium was found in the sun's atmosphere nearly 30 years before it was isolated and identified on earth. In 1868 when a spectroscope was first used at an eclipse, the spectrum revealed the presence of a series of yellow lines. These lines were different from the sodium lines already known and were of different wave length from any known. It was concluded that the lines were caused by some new element glowing in the sun's heat. This unknown element was promptly named helium (the sun). The "ium" ending indicates that the new element was thought to be a metal.

In 1891, Hillebrand, an American chemist, observed that certain minerals contained small quantities of an unreactive gas. He supposed it might be nitrogen and dismissed further consideration. Ramsay reinvestigated the gas and in 1895 showed it to be a new element and further showed it to have the spectral lines observed in the sun's spectrum in 1868. The new element fell heir to the name helium.

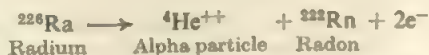
With the finding of both helium and argon and the placing of them next to hydrogen and chlorine in the Periodic Table, (Table ~ 5) it was apparent to Ramsay that three or four more of these elements should exist to fill in the spaces in table below:

Table 7.5.

																	H	He
Li	Be											B	C	N	O	F	1	
Na	Mg											Al	Si	P	S	Cl	Ar	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	2	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	3	
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	4	
		Lu																
Fr	Ra	Ac																
		Lw																

With this in view, he began an intensive investigation of air, and in 1898 with Travers he found three of the group: neon, krypton and xenon.

Near the turn of the century it was found that not only helium but also a heavier gas was accumulated around decaying radium. This gas was named radon.



Ramsay did not discover radon, but he did much towards determining its properties. A tribute might properly be made to Ramsay who had a hand in

the discovery and identification of each element. The precision of his work becomes apparent when one realizes how little of the individual gases appears in air (Table 7.6).

**Table 7.6. Composition of Dry Air in Per Cent by Volume**

Nitrogen	78.09	Neon	0.0018
Oxygen	20.95	Helium	0.00053
Argon	0.93	Krypton	0.0001
Carbon dioxide	0.03	Xenon	0.000009

#### SOURCES, PROPERTIES AND USES OF THE INERT GASES

Despite the low percentages, air is the source of all the inert gases with the exception of helium and radon, although they also occur in some volcanic gases. Natural gas often bears a substantial amount of helium (0.5 to 1.5% by volume) and is its commercial source. It is estimated that, if the demand were sufficient, 18 million cubic feet could be produced annually. Radon is obtained in only small amounts from decaying radium, and, because it is radioactive itself, it is used in small vials for treatment of cancer.

All of these elements are colorless, odorless gases. Some of their physical properties are tabulated below:

**Table 7.7. Physical Properties of the Inert Gases**

	Atomic Weight	Boiling Point	Freezing Point	Solubility in Water ml/L at 20 °C	Electrons in the Outermost Level
Helium	4.0026	-268.9	-272.1(?)	13.8	2
Neon	20.183	-246	-248.73	14.7	8
Argon	39.948	-185.8	-189.3	37.9	8
Krypton	83.80	-151.9	-169	73	8
Xenon	131.30	-109.3	-140	110.9	8
Radon	222	-62	-71	—	8

Helium is unique among all elements in that it will form a true solid only under a pressure of about 25 atmospheres. There is so little attraction between atoms that they will not hold together, even when almost motionless.

The noble gases are the most chemically inactive group of elements in the Periodic Table. The atoms do not pair to form molecules, and they form no compounds among themselves. In fact, until 1962 no bona fide compounds of the gases were known. Some helides (helium-containing compounds) had been reported; some hydrates had been detected, but these were not com-



pounds in the accepted sense. The noble gases were called "inert" gases as an indication of chemical inertness toward all other substances.

In 1933 Linus Pauling predicted the stability of some fluorine compounds of the higher atomic weight noble gases but no one prepared them. Early in 1962 Neil Bartlett identified the compound,  $O_2 PtF_6$ , which occurred as a direct combination of oxygen with the very reactive gas, platinum hexafluoride. Knowing that molecular oxygen had an ionization potential approximately that of xenon, he mixed xenon and the hexafluoride and obtained a compound of this formula,  $Xe PtF_6$ . Chemists at the Argonne National Laboratory quickly repeated Bartlett's experiments confirming his results. Further, upon decomposing the hexafluoride with heat, they suspected formation of a xenon fluoride compound. They then attempted to form the xenon fluoride compound directly. By heating xenon and fluorine gas together for one hour at 400°C then cooling to dry-ice temperature a white crystalline solid appeared which proved to be xenon tetrafluoride,  $XeF_4$ , a stable crystalline solid (in the absence of moisture) with a melting point of about 114°C.

With the confirmed discovery of noble gas compounds, many laboratories entered the field. Xenon difluoride, xenon hexafluoride, and tetrafluorides of radon and krypton have also been prepared. Hydrolysis with water has yielded, among other products, an oxyfluoride of xenon,  $XeOF_2$ , and the explosive trioxide  $XeO_3$ .

Although the preparation of noble gas compounds has been hailed as one of the great modern advances in inorganic chemistry, the gases as a group must be regarded as very inactive. Only the most active non-metals, fluorine and oxygen, have yet been found to combine with the gases. There is little likelihood that many stable compounds will be prepared.

The elements of group zero in the Periodic Table can be said to have two properties in common: high volatility (all are gases at room temperature) and *chemical inactivity*. These properties appear to be related to the structural similarity between the gases. Each gas, except helium, has an outermost level electron number of 8 (helium has a complete first shell of 2). The electrons are held tightly to the atom, leaving little electrical field to attract atoms together. Held tightly, the electrons are not easily lost to other atoms to form ionic bonds nor are they attracted to be shared by other than the most electro-negative atoms. The stability of the complete electron octet of the noble gases is repeated in the assumed electron configuration of other atoms as they react to form compounds.

Helium has been used in lighter-than-air craft. It has almost the same lifting power as hydrogen and is not flammable. It is blown around magnesium parts in welding. Heated magnesium will burn in air, but in an atmosphere of helium will not. Helium is mixed with oxygen and used in certain respiratory diseases. Its tiny atoms find their way through obstructions and assist the circulation of oxygen.

Neon is used in neon fluorescent signs. Red neon signs contain neon gas. Neon signs of different colors: blue, green, etc., have painted tubes or contain the right mixture of argon or mercury with the neon. Argon is used in

ordinary light globes. The glowing filament will not burn with the argon, and the argon atmosphere prevents the rapid sublimation of the white hot filament onto the glass walls of the bulb. The other two gases, krypton and xenon, are so rare that they have little commercial use.

### 3. ELECTROVALENT OR IONIC BONDING

The study of ionic bonding will be initiated by examining a simple ionic compound, table salt.

Table salt is a white solid composed of small cubic crystals, having a density of  $2.18 \text{ g cm}^{-3}$ . Salt melts sharply at  $804^\circ\text{C}$ , is soluble in water, and has a characteristic taste.

Repeated analyses show it to be 40% sodium and 60% chlorine. Therefore, the substance is a compound. It obeys the law of definite proportions. The calculation to follow gives the formula.

For each gram-atomic weight (23 g) of sodium there are

$$\frac{23 \text{ g}}{40 \text{ g}} \times 60 \text{ g} = 35.5 \text{ g (1 gram-atomic weight) of chlorine}$$

NaCl

Table salt is the simple, binary (two element) compound, NaCl. Let us consider electrolysis of molten salt. The cell diagramed in Figure 7.1, filled with salt, is placed in a furnace at a temperature greater than  $804^\circ\text{C}$ . Immersed in the melt, one at each end of the cell, are two graphite electrodes connected to the opposite poles of a storage battery (similar to the one in your automobile). The electrode connected to the (+) pole of the battery is called the anode; the cathode is connected to the (−) pole. A divider, perforated below the surface, separates the cell into the anode and cathode compartments.

When the circuit is closed, one can make the following observations: (1) an electric current flows through the external conductor (the wire) as noted on the ammeter. (2) A greenish yellow gas bubbles up around the anode and escapes. This gas, chlorine, is very poisonous. (3) A liquid silver pool of molten metal appears and floats on the surface of the salt in the cathode compartment. This metal is sodium. (4) The level of the molten salt drops. Salt is being consumed.

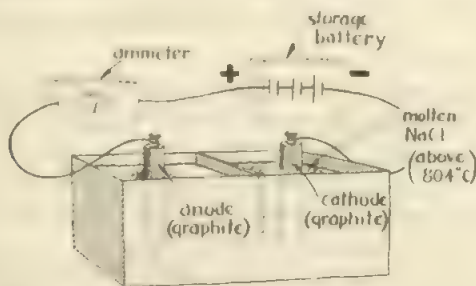


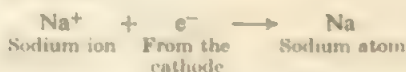
Figure 7.1. Diagram of an electrolysis cell for table salt.

These questions arise: (1) Why does sodium accumulate at the cathode? And how is it released from the compound? (2) Why does chlorine appear at the anode? And how is it released? (3) How is the electric circuit completed through the melt?

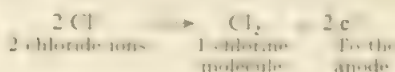
These questions are answered quite reasonably by the ionic theory. This theory tells us that the sodium "atom" in the compound bears a  $+$  charge. It has a plus charge because in the compound formation, one of its electrons is lost to a chlorine atom, which consequently carries a negative charge. When the circuit of the electrolysis cell is closed and the cathode becomes negative, the positive sodium "atoms," called ions, are attracted toward it. Simultaneously the negative chloride ions migrate towards the positive anode.

Upon arriving at the cathode each sodium ion gains an electron, becomes an atom and rises to collect with others as a pool at the surface. Upon arriving at the anode, each chloride ion loses an electron to the anode (is neutralized), pairs with another chlorine atom and escapes as a molecule of chlorine gas. The process occurring at the electrodes may be represented by the following equations:

#### Cathode



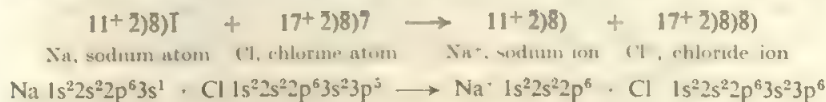
#### Anode



The reactions explain the existence of an electric current, the flowing of a stream of electrons, from the anode to the cathode through the wire, ammeter and battery. Electrons are taken up from the chloride ions by the anode and flow through the circuit to replace electrons at the cathode, where they are taken by the sodium ions. The number of electrons given up by the chloride ions must then be equal to the number absorbed by the sodium ions.

In the discussion of theory above, a charge of  $+1$  was assumed for each sodium ion and a charge of  $-1$  for each chloride ion. Careful studies of this electrolysis experiment show that 1 gram-atomic weight of sodium and 1 gram-atomic weight of chlorine are liberated with the passage of 96,500 coulombs (or  $6.02 \times 10^{23}$  electrons) of electricity. This is 1 electron per ion.

The preceding experiment and resultant discussion were given to show why it is assumed that in the melt (and the solid) of NaCl, all the sodium exists as sodium ions,  $\text{Na}^+$ , and all the chlorine exists as chloride ions,  $\text{Cl}^-$ . In the formation of one formula of NaCl from the atoms, an electron is transferred.



In "kernel" form



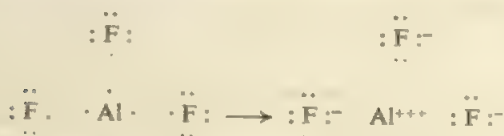
Observe, sodium in combining has assumed the same electron arrangement as neon (2 8). The chloride ion assumes the same electron arrangement as argon (2 8 8). A further indication of the stability of the inert gas or octet configuration is found in the fact that sodium is found in nature as  $\text{Na}^+$  in compounds. Sodium is never found uncombined. Furthermore, considerable energy is required to take the electron from the chloride ion and transfer it to the sodium. In this case, electrical energy was consumed from the battery. Other examples of ionic compounds with electron arrangements are shown below. In each case the "octet" or "inert gas" structure is attained by the ions in the compound.

EXAMPLE 1. Write the electronic structure and the formula of magnesium chloride



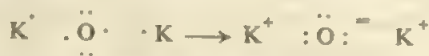
Answer:  $\text{MgCl}_2$

EXAMPLE 2. Find the formula of aluminum fluoride.



Answer:  $\text{AlF}_3$

EXAMPLE 3. Find the formula of potassium oxide.



Answer:  $\text{K}_2\text{O}$

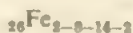
You will notice in the examples cited that magnesium, aluminum and potassium atoms have a different capacity in combination. The capacity is called valence. Potassium has an ionic valence of +1, magnesium, of +2 and aluminum of +3. The valence is equal to the charge on the ion, it is also equal to the number of electrons lost in compound formation. Oxygen has an ionic valence of -2; and chlorine and fluorine, of -1. This valence is equal to the number of electrons gained by the chlorine in compound formation; it is equal to the charge on the ion, and to 8 minus the number of electrons in the valence shell.

One can find the ionic valence of the elements that appear in the right and left extremes of the Periodic Table. The group number, the Roman numeral



above the vertical columns, is the number of electrons in the outermost shell of the group. For example calcium is in Group II, has two valence electrons, and has an ionic valence of  $+2$ . Oxygen is in Group VI, has 6 valence electrons, must gain 2 electrons in ionic combination and has an ionic valence of  $-2$ .

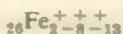
Among the transition elements, the determination of ionic valence is more difficult due to an added complication. Consider iron, atomic number 26, with the electron configuration represented below. Two well-known iron oxides exist: ferrous oxide,  $\text{FeO}$ , and ferric oxide  $\text{Fe}_2\text{O}_3$ . In both compounds oxygen has a valence of  $-2$ , that is, it requires 2 electrons to complete the inert gas configuration. In ferrous oxide, whose atoms are 1 to 1, iron has a valence of  $+2$ . In ferric oxide whose atoms are 2 to 3, the valence of iron is  $+3$ . Consideration of the electronic structure of iron



indicates that the ferrous ion formed by the loss of 2 electrons is the ion expected,



but the ferric ion also occurs:



One of the electrons in the next outermost level takes part and is lost in the ionic bonding. Again this accents the stability of the octet configuration. The number 14 is not a stable number and one of the electrons can be lost. In all the transition elements, the number of electrons in the next outermost level is between 9 and 18 inclusive, never 8. One or two of these may participate at times, giving them a variable valence. Even the number 18, when it fills the shell, is not so stable as 8; copper ( $2-8-18-1$ ) has two ions:  $\text{Cu}^+$  and  $\text{Cu}^{++}$ . Once the electrons are transferred and ions are formed, they are charged. By virtue of the charge, they are held together  $+$  to  $-$  and  $-$  to  $+$ . Each ion is quite independent of the others. In a melt the ions move around each other and migrate to opposite poles in an electrolysis cell. In a solid they line up like a stack of mismatched checkerboards. A sodium chloride crystal appears somewhat as represented below (Fig. 7.2).

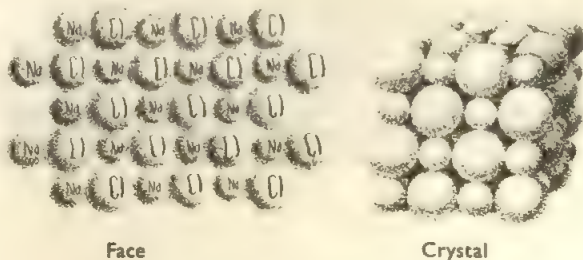


Figure 7.2. Diagram of a sodium chloride crystal.

Pick out any sodium ion,  $\text{Na}^+$ , in the interior of the crystal. There are four chloride ions,  $\text{Cl}^-$ , about it in the plane. Also, there is a  $\text{Cl}^-$  in front and one in back. In other words, about each  $\text{Na}^+$  there are 6 closest  $\text{Cl}^-$ 's. There is no special bond with any one of them. About each  $\text{Cl}^-$  in the crystal there are 6 closest  $\text{Na}^+$  ions. There is no pairing of atoms, there are no molecules, just the alternating  $+$  and  $-$  ions, attracted and held next to one another because of those plus and minus charges.

#### 4. COVALENT BONDING

The study of covalent bonding will be introduced by discussing an example. The substance to be considered is hydrogen chloride.

Pure hydrogen chloride is a colorless gas at room temperature with an acrid, biting odor. Its boiling point is  $-84.9^\circ\text{C}$  and it freezes at  $-114.8^\circ\text{C}$ .

Hydrogen chloride may be formed by direct combination of its elements. The two gases burn together. At all times they combine in the proportion of 97.3% chlorine and 2.7% hydrogen by weight. Hydrogen chloride is therefore a compound. The formula is determined below.

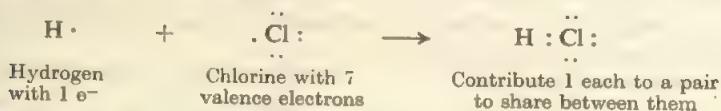
For each gram-atom weight (1.0 g) of hydrogen, there is:

$$\frac{1 \text{ g}}{2.7 \text{ g}} \times 97.3 \text{ g} = 35.5 \text{ g (1 gram-atomic weight) of chlorine}$$

HCl

Unlike table salt, hydrogen chloride is a non-conductor of electricity. When dissolved in water, it becomes a good conductor, but the pure substance conducts no current either as a liquid or as a gas. This suggests that there are no ions present. Studies with gases (to be discussed in a later chapter) show the gas to be composed of molecules, represented by HCl, containing 1 atom of each element.

It is postulated that the two atoms in the molecule share a pair of electrons, binding them together and completing valence electron shells to inert gas configurations.

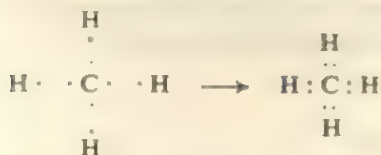


Hydrogen now has a share of 2 electrons, and has the helium configuration. Chlorine with the shared pair has the neon configuration.

The shared pair is not held stationary between them, but occupies an orbit about both nuclei, whereas the other 3 pairs move about chlorine alone.

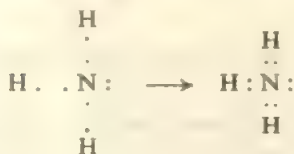
The structures of several other covalent compounds are diagramed below. The atoms will be shown first in "kernel" form and will then be placed together.

a. Methane,  $\text{CH}_4$

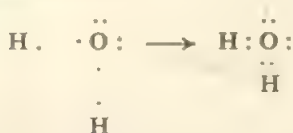


In methane each hydrogen atom holds 2 electrons (helium structure). Carbon holds 8. Incidentally, the methane molecule is not flat but three dimensional; two of the hydrogen atoms lie out of the plane of the paper.

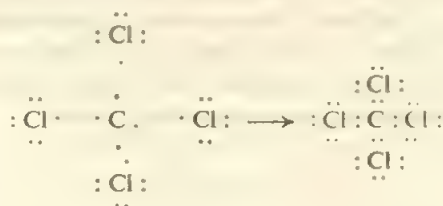
b. Ammonia gas,  $\text{NH}_3$



Again, each hydrogen holds two electrons; nitrogen, 8.

c. Water,  $H_2O$ 

d. Carbon tetrachloride,  $\text{CCl}_4$



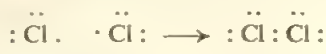
While the experimental evidence for the fact has not been cited yet, one can see that it is reasonable for the elemental gases to contain diatomic molecules, such as  $H_2$ ,  $Cl_2$ ,  $O_2$  and  $N_2$ .

a. Hydrogen gas,  $\text{H}_2$



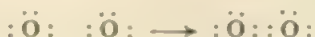
Only by sharing can the inert gas (helium type) electron configuration be reached by hydrogen atoms. This allows hydrogen to be sufficiently unreactive to exist as a gas.

b. Chlorine gas,  $\text{Cl}_2$



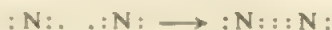
Again the octet configuration is reached, giving stability to the gas. The bond here, as is the case with all covalent bonds studied thus far, is a *single bond*. Two shared electrons constitute a single covalent bond.

c. Oxygen gas,  $O_2$



Two oxygen atoms gain stability by sharing 4 electrons, two from each atom. This bond is called a *double covalent bond*.

d. Nitrogen gas,  $N_2$



In the nitrogen molecule, 6 electrons are shared in one bond, making it a *triple bond*.

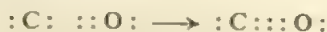
Covalent compounds may exhibit *multiple bonds*, as do some of the elemental gases.

a. Carbon dioxide gas,  $CO_2$



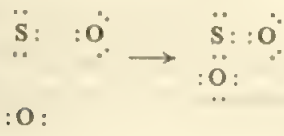
The carbon dioxide molecule has two double bonds.

b. Carbon monoxide, CO

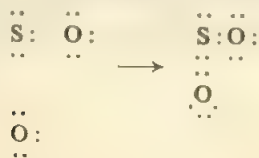


Carbon monoxide has 1 triple bond like nitrogen gas. This bond is not exactly like that for nitrogen, for here, oxygen and carbon contribute an unequal number of electrons, 4 and 2, to the 6 held jointly. Two atoms tend to contribute equally to any covalent bond between them; when this is impossible one atom may contribute an extra pair of electrons.

c. Sulfur dioxide,  $SO_2$



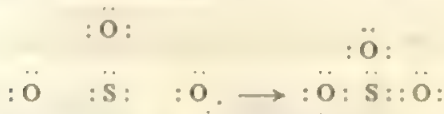
Sulfur dioxide, by the simple electron-pair-sharing picture, appears to have one single coordinate covalent bond and one double covalent bond. As can be seen, the molecule could also be:





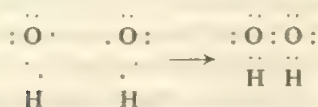
Obviously, this molecule is the same as the first, but different oxygen atoms appear to have different bonds. Of course, the electron energies of the total molecules are the same. It so happens that when two equivalent electron structures can be drawn for a molecule or ion, the real structure is neither but is somewhat in between the two. The molecule is called a *resonance hybrid*. The S to O bonds in sulfur dioxide are identical; both are shorter than a single bond; both are longer than a double bond. The extra pair of electrons represented by the double bond occupies an orbital over the entire molecule and serves to draw the whole together.

d. Sulfur trioxide,  $\text{SO}_3$



It is obvious that one can draw two more equivalent structures for sulfur trioxide. The molecule is therefore a resonance hybrid and the three S to O bonds are identical. All are shorter than single bonds.

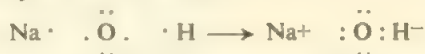
e. Hydrogen peroxide,  $\text{H}_2\text{O}_2$



Three pairs of binary compounds of the same two elements have been discussed in this chapter: CO and  $\text{CO}_2$ ,  $\text{SO}_2$  and  $\text{SO}_3$ , and  $\text{H}_2\text{O}$  and  $\text{H}_2\text{O}_2$ . Here the valence becomes difficult to determine, as was the case with transition metals whose valence cannot be predicted.

Furthermore, even among the transition elements, the valence was the number of electrons lost, whether or not they came solely from the valence shell. No direct significance can be given to a statement that the valence of carbon is +4 and the valence of oxygen is -2 in carbon dioxide, or the statement that the valence of carbon is +4 and hydrogen +1 in methane. For this reason we will leave the discussing of covalent valence (more properly called oxidation state) to a later chapter.

Some compounds exhibit both types of bonding. Consider the white solid, sodium hydroxide ( $\text{NaOH}$ ):



The sodium atom loses its electron and becomes an ion. Hydrogen and oxygen each contribute an electron to a pair shared in common. Together they are an ion, a complex ion, also called a radical.

A covalent bond exists between the O and H. An ionic bond exists between the  $\text{Na}^+$  and the  $\text{OH}^-$  as a whole. There is no special bond between  $\text{Na}^+$  and O. The two ions are attracted together because of their opposite charges.



and non-metals. The metals may combine with the non-metals to form ionic compounds. Non-metals may also take part in covalent bonding.

Of considerable interest is the nature of the covalent bond between atoms in a molecule or a complex ion. Examples of specific bonds will be illustrated to teach general principles.

(a) *The bond in a chlorine gas molecule*

As stated previously, each chlorine has 7 valence electrons [it contains 2 in the first sublevel (in the spherical s-orbital) 2 in each of 2 p-orbitals of the second sublevel but only 1 in one "dumbbell" shaped orbital]. Upon bond formation between the 2 chlorine atoms the orbitals of each atom containing but one electron come together to form one molecular orbital (one orbital around both chlorine kernels) as shown in Figure 7.3. The two electrons, one

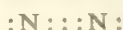


Figure 7.3. See text for explanation.

from each atom, occupy the molecular orbital. The molecular orbital represents the fact that the negative electrons have the highest probability of appearance between the positive nuclei and thus draw them together. An orbital along the axis between the two nuclei is called a  $\sigma$  (sigma) orbital, as are the electrons that occupy it and form the bond. All single bonds are sigma bonds.

Multiple bonds (double and triple bonds) are more complicated.

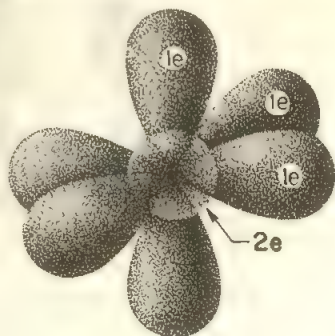
(b) *Consider the bond in the nitrogen molecule represented by*



Each nitrogen atom contains 5 valence electrons: 2 in the 2s-orbital (completing the subshell) and 1 in each p-orbital of the second sub-shell (Fig. 7.4).

When the 2 atoms are joined together, one pair of atomic p-orbitals (one from each atom) merge to form a sigma bond (Fig. 7.5). The other p-orbitals containing only one electron come together in pairs (one from each atom),

Figure 7.4. N-atom.



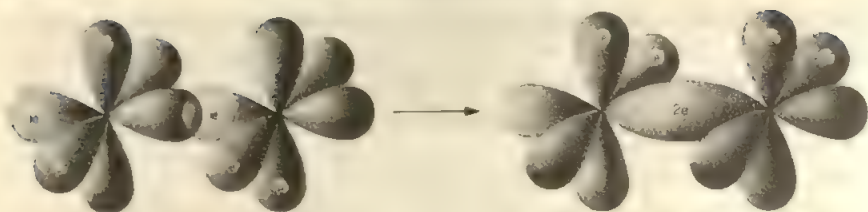


Figure 7.5. The sigma bond in nitrogen.

sidewise, to form one orbital above and below and one before and behind the molecular axis, each orbital containing 2 electrons (Fig. 7.6). These

Figure 7.6. The  $\pi$ -bonding orbitals of  $N_2$ .

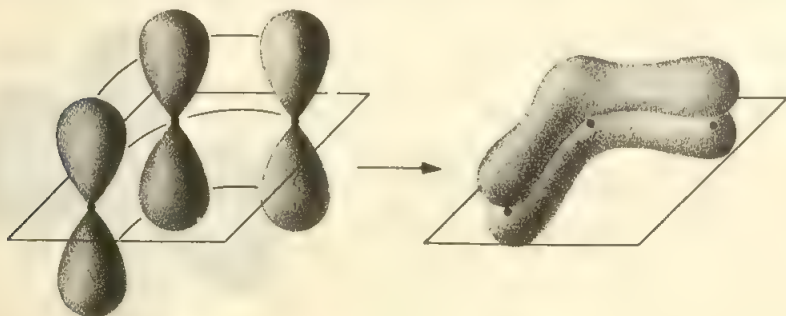
orbitals above and below (and front and back) are called  $\pi$  (pi) orbitals. When occupied by 2 electrons the orbital makes a  $\pi$ -bond. The triple-bond in the nitrogen molecule is composed of one sigma and two pi bonds.

The pi bonds (pi-orbitals containing electrons) are susceptible to and attracted by approaching positive groups. The distortion of the pi bond with the approach of charged groups accounts for many multiple bond reactions in organic chemistry and will be discussed considerably in latter portions of the text.

(c) The two bonds in the sulfur dioxide molecule,  $S : O$  are identical



although the electronic structure does not indicate it. The 2 electrons in the one apparently double bond occupy a  $\pi$ -orbital spread above and below the whole molecule (Fig. 7.7). The 2 electrons in the pi orbital hold the 3 positive kernels together and, therefore, contribute only half strength to each S to O bond. With the sigma bond, the bond is a  $1\frac{1}{2}$  order bond.

Figure 7.7.  $SO_2$  molecule.

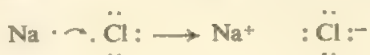


## 5. ELECTRONEGATIVITY

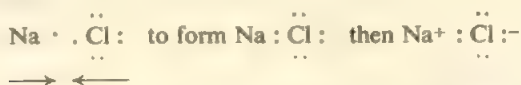
The preceding discussions indicate that the chemical properties of an element are primarily dependent upon the electron configuration of its atoms. More specifically these properties are determined by the valence electrons, those that are gained, lost or shared in bond formation. In almost all cases the gaining, losing and sharing of these electrons results in an inert gas electron configuration. It is not to be supposed that the electrons feel lonely when there are fewer than 4 holding outposts about an atom. Nor is it likely that they find a special congeniality when 8 are present about the kernel of an atom. Electrons are charged particles and their behaviour in chemical reactions is controlled by the electrostatic forces acting upon them. An electron does not leave an orbit in one atom to occupy one in another unless the second attracts it more strongly. Neither will an electron pair be held jointly by 2 atoms unless each atom has a great and nearly equal attraction for them.

In the formation of table salt from its elements, electrons are transferred from sodium atoms to chlorine atoms. It is incorrect to assume that an electron flees from a sodium atom, seeks out a chlorine atom and finds refuge in its orbit. Reaction occurs only after the two atoms collide with a sufficient force that the valence orbits of the two atoms become engaged. Momentarily a covalent bond exists with the electron pair in the orbits of both atoms. However, chlorine has much greater attraction for electrons in the valence level than does sodium, and consequently pulls the electron to itself.

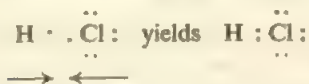
Not this:



But this:



The formation of hydrogen chloride from hydrogen and chlorine atoms follows the same initial sequence. The atoms collide and the electrons orbits enmesh. But in this case both atoms have great attraction for electrons in their valence shells and the covalent bond persists.



It should be obvious that the type of bond to be formed between two atoms is controlled by the relative magnitude of the attraction each has for electrons in the valence shell. This attraction is known as electronegativity. A study of the electronic structures of the atoms will reveal the variations in electronegativity.

Consider the electron arrangement of the atoms of elements sodium to argon. These elements comprise the second row of 8 in the Periodic Table. All the atoms in the series have the same kernel of electrons, the completed quantum levels of 2 and 8. They differ in the charge on the kernel and the number of valence electrons. Beginning with the sodium atom, one positive

charge on the kernel attracts the lone valence electron as it moves in its orbit (Fig. 7.8a). Compare the forces acting on this electron with those acting on each of the electrons of the magnesium atom (Fig. 7.8b). In the argument it is assumed that all the valence electrons possess the same energy, follow circular orbits of the same diameter, and that the valence electrons of the same atoms stay (due to mutual repulsion) as far from one another as possible. These assumptions are not strictly correct, but give a model sufficiently correct and simple enough to work with.

In the magnesium atom each electron is attracted toward the kernel with two plus charges as against one in the sodium atom. At the same time the

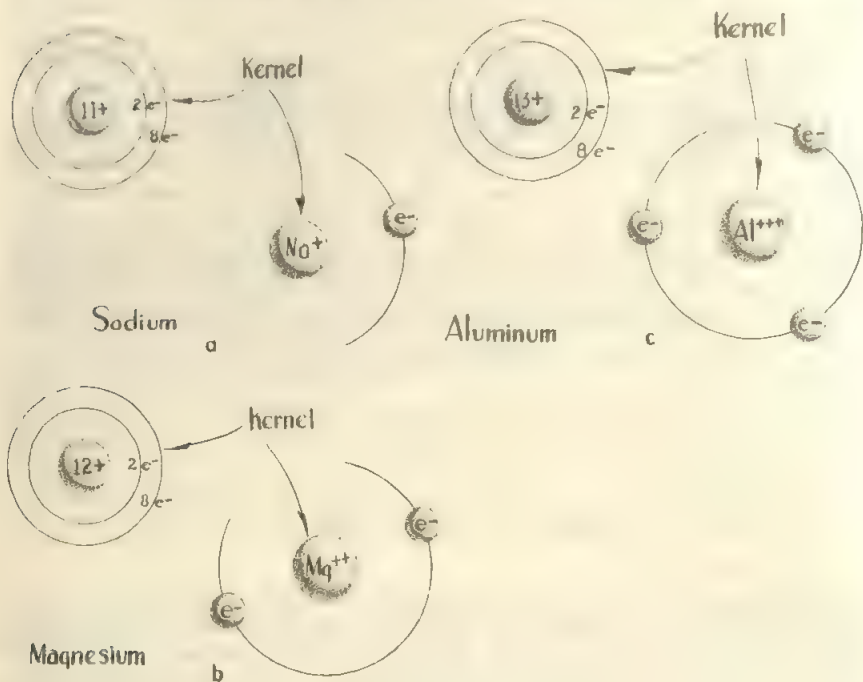


Figure 7.8. Valence electron structures.















two electrons repel each other, tending to counteract the additional attraction. But since the distance between them is twice the distance from each to the nucleus, the repulsion is only a fraction of the increased attraction, and magnesium holds each of its electrons more firmly than sodium holds its one. Magnesium is more electronegative than sodium.

The next element, aluminum (Fig. 7.8c), has 3 valence electrons. In moving from magnesium to aluminum, one more positive charge has been added to the kernel to attract each valence electron, and a third electron has been added to form an equilateral triangle with the other two. Again the positive charge added to the kernel is nearer the valence electrons than the negative charge of the third electron, and the electronegativity increases. One can extend this argument step by step across the Periodic Table to show

that electronegativity increases regularly from sodium to argon. It may also be applied with the same result to the first row of 8 and to all other portions of rows where there is an increase in the number of valence electrons from left to right. It cannot be applied to a transition element series such as the one from scandium to zinc, for these atoms differ only in the number of electrons in the kernel. However, one might predict from the argument that the electronegativities of these atoms should be nearly the same. This is true.

Table 7.9 lists the electronegativity values for the two rows of elements—lithium to fluorine and sodium to chlorine—as determined by Pauling. Also tabulated are the radii of the atoms in the solid state and the “average” ionization potential. These are included as experimental evidence that the electronegativity values are assigned correctly.

**Table 7.9. Electronegativities and Atomic Radii**

	<i>Li</i>	<i>Be</i>	<i>B</i>	<i>C</i>	<i>N</i>	<i>O</i>	<i>F</i>
Electronegativity	1.0	1.5	2.0	2.5	3.0	3.5	4.0
							
Radius Å	1.23	0.889	0.80	0.77	0.74	0.74	0.72
“Average” Ionization Potential	5.39	13.76	23.79	36.99	53.38	72.17	94.11
	<i>Na</i>	<i>Mg</i>	<i>Al</i>	<i>Si</i>	<i>P</i>	<i>S</i>	<i>Cl</i>
Electronegativity	0.9	1.2	1.5	1.8	2.1	2.5	3.0
							
Radius Å	1.57	1.36	1.25	1.17	1.10	1.04	0.994
“Average” Ionization Potential	5.14	11.34	17.42	25.77	35.71	46.1	58.4

The volume of an atom in the solid state is found by dividing the solid volume of one gram-atomic weight of the element by Avogadro's number. The radius is calculated from the volume. One can see that from lithium to fluorine and from sodium to chlorine each succeeding atom is smaller than the one before, even though one more electron has been added. This would mean that the valence electrons are held more closely because their orbits determine the size of the atom.

The ionization potential is a measure of the energy required to remove an electron from an atom in the vapor state. The apparatus used to measure the ionization potential of an element contains a fluorescent tube of that element. Electrons are shot into the vapor from cathode to anode with a gradually increasing voltage while the current through the tube is being monitored. At first, collision of the cathode rays (electrons) with the atoms merely raises the

electron to higher orbits within the atoms, and the gas fluoresces. But eventually the cathode rays gain sufficient energy to remove electrons completely from the atoms. At this point the positive ions formed assist in carrying the electric current through the tube and a sharp increase in amperage occurs. The voltage at which the current increases is called the ionization potential. Additional increases in amperage occur as the electrons gain sufficient energy to remove the second, third and fourth electrons. The ionization potential is given in volts and is proportional to the energy required to remove the electron. The "average" ionization potential used in Table 7.9 is an average of the ionization potentials for each of the valence electrons. For sodium and lithium it is the first ionization potential. It is an average of 2 values for beryllium and magnesium, etc. The average" ionization potential increases from left to right in both rows of Table 7.9 following the trend of increasing electronegativity.

Consider the elements of a family in the Periodic Table, Group I: lithium, sodium, potassium, rubidium and cesium. Each of these atoms has one valence electron. Each electron is attracted to the kernel with a charge of  $+1$  and should be held to the kernel with the same force. But each succeeding atom has one more shell of electrons (Table 7.10). Each atom is bigger as one

**Table 7.10. The Alkali Group Atoms**

<i>Electron Configuration</i>	<i>Size-Radius Å</i>	<i>Ionization Potential</i>
Li 2-1	1.22 ○	5.37
Na 2-8-1	1.57 ○	5.14
K 2-8-8-1	2.025 ○	4.32
Rb 2-8-18-8-1	2.16 ○	4.16
Cs 2-8-18-18-8-1	2.35 ○	3.88

proceeds down the group. The sizes of the atoms appear in Table 7.10. As the distance between the nucleus and electron increases, the attraction decreases and electronegativity decreases down the group from lithium to cesium. The ionization potentials are shown to decline with the electronegativity, in the same table.

The kernel notation for hydrogen is similar to those of the first group. One might assume that hydrogen should have an electronegativity a little greater than that of lithium. However, the radius of the atom is so small that the ionization potential is increased to 13.60 volts and the electronegativity is 2.1, a bit greater than that of boron.

The electronegativities of certain elements of the Periodic Table are shown in Table 7.11. The electronegativity increases from bottom to top and from left to right in the table, with hydrogen occupying a position just to the right of boron. As a device to aid memory, one may arrange the elements as in



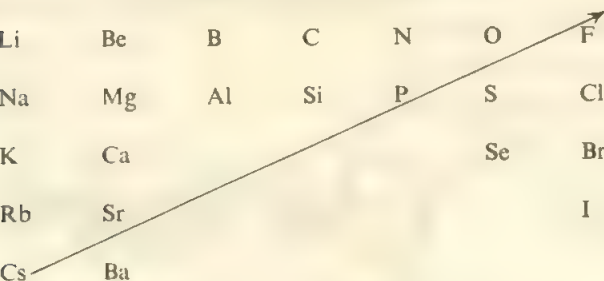
**Table 7.11. Electronegativity of the Elements**

		H 2.1				
Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0				Se 2.4	Br 2.8
Rb 0.8	Sr 1.0					I 2.4
Cs 0.7	Ba 0.9					

Table 7.12, then draw an arrow from cesium to fluorine. Of all the elements that form bonds, fluorine is the most electronegative and cesium is second only to rare francium in being the least electronegative. Electronegativity increases diagonally up and from left to right across the table. This explains

**Table 7.12. Arrow Points in the Direction of Increasing Electronegativity**

Li	Be	B	C	N	O	F
Na	Mg	Al	Si	P	S	Cl
K	Ca				Se	Br
Rb	Sr					I
Cs	Ba					



why the zigzag line separating metals from non-metals (Table 7.8) is not vertical. It separates those atoms with too little attraction to hold electrons in reaction from those with sufficient energy to either gain or share.

### POLAR BONDS AND POLAR MOLECULES

Consider the hydrogen molecule,  $H_2$



Each hydrogen nucleus has a charge of  $+1$ . Each hydrogen shares  $1/2$  of 2 electrons and therefore each end of the molecule is neutral. Suppose one

could shift the pair of electrons one-half the way toward the hydrogen on the right.

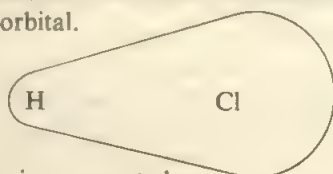


Then the H on the right would have  $\frac{3}{4}$  share of 2 electrons; the H on the left  $\frac{1}{4}$  share of 2 electrons and the molecule would have a charge of  $-\frac{1}{2}$  on the left and  $+\frac{1}{2}$  on the right. This cannot happen with the hydrogen molecule, but it does with hydrogen chloride.

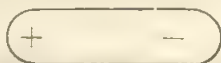


The other three pairs of electrons held solely by chlorine are not shown. Chlorine is more electronegative than hydrogen and pulls the shared electrons closer. The Cl atom has a kernel charge of  $+7$ , holds 6 electrons completely, and has more than  $\frac{1}{2}$  share of the electron pair. Thus the molecule at that end has a small negative charge. The H atom has a nuclear charge of  $+1$ , has less than  $\frac{1}{2}$  share of the two electrons, and carries a small  $+$  charge.

The electron pair is not removed completely from the hydrogen, and has an orbital about both nuclei, but the orbital is distorted so that the chlorine has a greater share of the orbital.



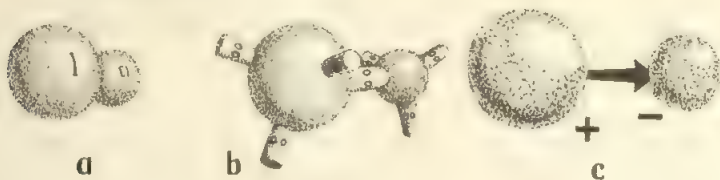
At times such a molecule is represented as:



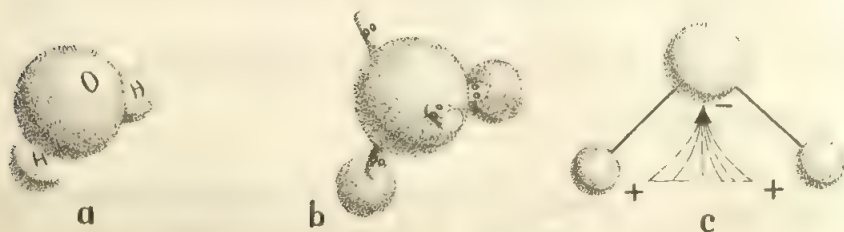
The charges at the ends of the molecules have been likened to the north and south poles of a magnet. The bond is called a polar bond. The molecule is a polar molecule, or a dipole.

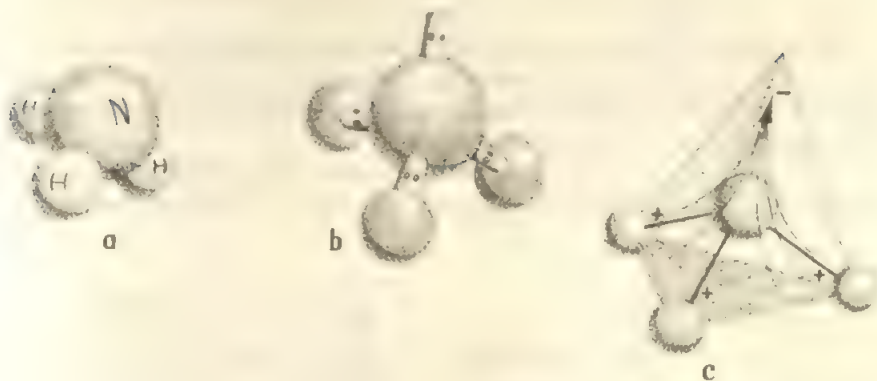
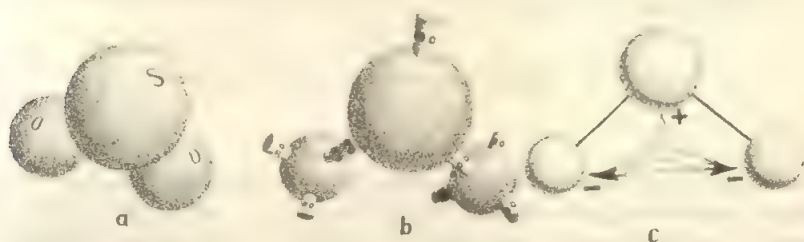
Other polar molecules are:

### 1. Iodine monochloride, $\text{ICl}$

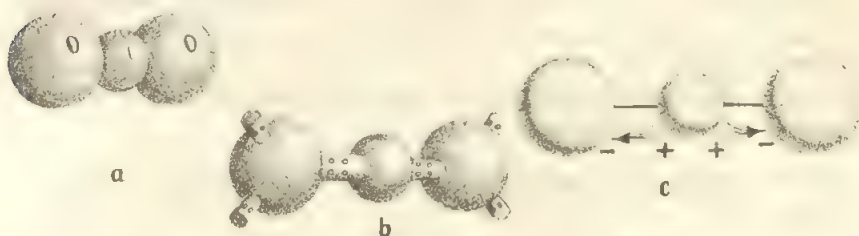


### 2. Water, $\text{H}_2\text{O}$



3. Ammonia,  $\text{NH}_3$ 4. Sulfur dioxide,  $\text{SO}_2$ 

Some non-polar molecules with polar bonds are these:

5. Carbon dioxide,  $\text{CO}_2$ 

Polar effects are opposite and equal and cancel each other.

6. Carbon tetrachloride,  $\text{CCl}_4$ 

Each C—Cl is polar, but the molecule is symmetrical, and no Cl is more negative than another.

The polarity of molecules can be demonstrated and measured by an electrical apparatus called a condenser. A condenser is composed of two parallel metal plates mounted closely together. The two plates are connected to opposite poles of a battery (Fig. 7.9a).

When the key is closed, a surge of current flows through the wire, pulling electrons (—) from the left plate to the right plate. If the plates are moved

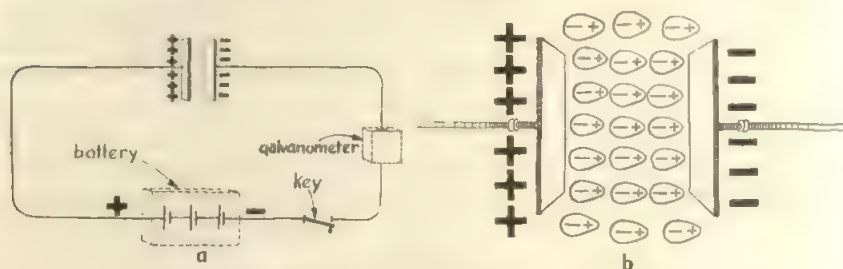


Figure 7.9. Diagram of apparatus for measuring dipoles.

closer together, a greater charge can be placed on the plates with the same voltage, because the positive plate attracts the electrons across the void. The charge on the plates can also be increased if the air between the condenser plates is replaced with dry HCl gas. This can be explained if the molecules are polar. In the electrostatic field they tend to be oriented + to — and — to + (Fig. 7.9b). The + end of the molecules next to the negative plate attracts the electrons and makes it possible to place more there without changing the voltage. Replacing the HCl gas between the plates with air will cause a momentary reverse flow of electrons, restoring the charge on the plates to the value held originally with air.

Table 7.14. Dipole Moments in Debye Units

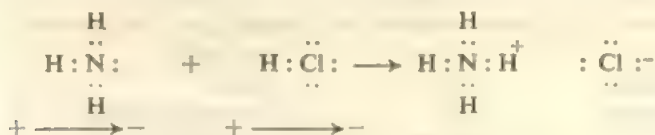
HCl	1.03	NH <sub>3</sub>	1.49
HBr	0.78	SO <sub>2</sub>	1.61
HI	0.38	CO <sub>2</sub>	0.0
H <sub>2</sub> O	1.85	CO	0.11
H <sub>2</sub> S	0.95		

Ammonia gas will increase the capacitance, the charge on the plates; so will sulfur dioxide gas. Hydrogen gas, chlorine gas, carbon tetrachloride vapors will not. By this method the dipole moments (relative polarity) of many substances have been measured. Some are tabulated in Table 7.14. These values agree with expected values. The difference in electronegativities between H and the other element decreases down the series HCl, HBr and HI, as does the measured dipole. The dipole of water is greater because



there are two polar bonds complementary to each other, etc. Check the rest of the series to see if you would anticipate the relative values.

The polarity of molecules accounts for many reactions and ion formations. For example, it explains why ammonia and hydrogen chloride gas approach negative end to positive end, then divide to give ionic ammonium chloride.



### BOND TYPE VS. PERIODIC TABLE

If a bond forms between similar atoms, electrons are shared equally ( $\text{Cl} : \text{Cl}$ ), and the bond is non-polar covalent. If the bond is between atoms somewhat similar, but not the same



electrons will be shared, but not equally. The bond is a polar covalent bond. Except for hydrogen, similar atoms share electrons only when each has 4 or more valence electrons. If the bond is between markedly dissimilar atoms with a great difference in electronegativity, electrons will be transferred and the bond is ionic.



### SALTS: FORMULAS AND NAMES

Many ionic compounds (salts) are encountered in inorganic chemistry. These compounds contain both simple and complex ions. The compound is named by the ions it contains, the positive ion first, the negative ion last. For example the compound  $\text{CuSO}_4$  contains cupric ions,  $\text{Cu}^{++}$ , and sulfate ions,  $\text{SO}_4^-$ . If one memorizes a list of the most common ions, he can name any compound from its formula, and from the name he can identify the ions present. Furthermore, knowing the charges carried by the ions and knowing that all compounds are neutral, one can write the formula from the name. For example, aluminum sulfate contains aluminum ions,  $\text{Al}^{+++}$ , and sulfate ions,  $\text{SO}_4^-$ . Because aluminum sulfate must carry no charge, the ions must appear in any crystal in the ratio of 2 to 3:

$$2 \times (+3) = 3 \times (-2)$$

The formula is  $\text{Al}_2(\text{SO}_4)_3$ .

Table 7.15 is a list of the most commonly appearing ions with their formulas. One should learn the names and formulas (including the charge) of all these ions.

**Table 7.15. Some Common Ions**

<i>Name</i>	<i>Formula</i>	<i>Name</i>	<i>Formula</i>
Acetate	$\text{C}_2\text{H}_3\text{O}_2^-$	*Hydroxide	$\text{OH}^-$
✓Aluminum	$\text{Al}^{+++}$	Iodide	$\text{I}^-$
*Ammonium	$\text{NH}_4^+$	✓Lead (plumbous)	$\text{Pb}^{++}$
✓Barium	$\text{Ba}^{++}$	Magnesium	$\text{Mg}^{++}$
*Bicarbonate	$\text{HCO}_3^-$	Manganous	$\text{Mn}^{+1}$
✓Bromide	$\text{Br}^-$	Mercurous	$\text{Hg}_2^{++}$
Calcium	$\text{Ca}^{++}$	Mercuric	$\text{Hg}^{++}$
*Carbonate	$\text{CO}_3^-$	✓Nickelous	$\text{Ni}^{++}$
*Chlorate	$\text{ClO}_3^-$	*Nitrate	$\text{NO}_3^-$
*Chloride	$\text{Cl}^-$	*Nitrite	$\text{NO}_2^-$
*Chlorite	$\text{ClO}_2^-$	Permanganate	$\text{MnO}_4^-$
Chromate	$\text{CrO}_4^-$	*Phosphate (ortho)	$\text{PO}_4^-$
✓Cupric	$\text{Cu}^{++}$	✓Potassium	$\text{K}^+$
Cupric ammonia	$\text{Cu}(\text{NH}_3)_4^{++}$	Silver	$\text{Ag}^+$
✓Cuprous	$\text{Cu}^+$	Sodium	$\text{Na}^+$
*Cyanide	$\text{CN}^-$	*Sulfate	$\text{SO}_4^-$
✓Ferric (iron)	$\text{Fe}^{+++}$	*Sulfide	$\text{S}^-$
✓Ferrous (iron)	$\text{Fe}^{++}$	*Sulfite	$\text{SO}_3^-$
Fluoride	$\text{F}^-$	Zinc	$\text{Zn}^{++}$

The elements marked by checks ✓ and asterisks \* are to be used in Problem 24 at the end of the chapter.

It may be noted that both chlorine and hydrogen appear in the upper right corner of the Periodic Table. This is true of covalent compounds. In the ionic compound represented, sodium is from the lower left of the table; chlorine from the upper right. This is true of all binary ionic compounds. A further rule might be stated: Elements in the first two groups at the far left of the table may take part in ionic bonding only.

It should be noted that a few compounds contain an atom without an octet configuration. These exceptions are few. Among these are nitric oxide (NO), nitrous oxide ( $\text{NO}_2$ ) and chlorine dioxide ( $\text{ClO}_2$ ).

Three simple rules may assist in memorization of Table 7.15.

1. Simple positive ions retain their elemental name unless there are two or more possible valences. When there are two positive ions differing only in charge, the ion of greater charge (valence) ends in *ic*; the ion of lesser charge in *ous*.
2. Simple negative ions end in *ide*.
3. Complex negative ions containing oxygen end in either *ate* or *ite*. When the negative complex ions differ only in the number of oxygen atoms they contain, the one with more oxygen atoms ends in *ate*, the one with fewer in *ite*.

1 Complete this portion of the Periodic Table by filling in atomic number, symbol, complete electronic configuration.

[illegible]

2. On what basis was the Periodic Table constructed originally?
3. What structural similarity exists among elements within a group (or family) of the Periodic Table?
4. Name the most important property of the inert gases.
5. In what way do the inert gases aid in a study of bonding?
6. Who had most to do with the discovery and identification of the inert gas elements?
7. What is interesting about the discovery, identification and naming of helium?
8. State four uses of the inert gases.
9. Compare the boiling points and freezing points of the inert gases (Table 7.7). Do they vary as you would expect?
10. Write the electronic configuration and show charges, where they exist, for:
  - a. The lithium atom and the lithium ion.
  - b. The fluorine atom and the fluoride ion.
  - c. Fe; Fe<sup>++</sup>, ferrous ion; Fe<sup>+++</sup>, ferric ion.
  - d. O<sup>-</sup>, F<sup>-</sup>, Ne, Na<sup>+</sup>, Mg<sup>++</sup> and Al<sup>+++</sup>.
11. What evidence is there that sodium and chloride ions exist in molten salt?
12. What does this anode reaction equation mean:  $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$ ?
13. How might one show experimentally that the charges on the sodium and chloride ions are +1 and -1 respectively?
14. Define ionic valence.
15. What correspondence is there between groups (or families) in the Periodic Table and ionic valence?
16. Explain why transition metals may exhibit more than one ionic valence.
17. Write the formulas for the following binary compounds from a knowledge of valence electron structures:
  - (a) sodium fluoride, (b) lithium oxide, (c) calcium nitride, (d) sodium hydride, (e) aluminum bromide, (f) barium oxide, (g) magnesium nitride.
18. Write valence electron structures (dot formulas) for:
  - (a) hydrogen gas, (b) nitrogen gas, (c) ammonia gas, (d) carbon tetrachloride, (e) ammonium ion, (f) hydroxide ion.
19. Define electronegativity. Using the table in Question 1, show how electronegativity varies.
20. Define: (a) polar bond, (b) polar molecule, (c) dipole.
21. What experimental evidence is there for the existence of polar molecules?
22. Which of the following contain polar covalent bonds?
  - (a) HCl, (b) H<sub>2</sub>O, (c) CO<sub>2</sub>, (d) CO, (e) NH<sub>3</sub>, (f) CCl<sub>4</sub>, (g) CH<sub>4</sub>, (h) HClO<sub>4</sub>, (i) NaCl, (j) Li<sub>2</sub>O, (k) N<sub>2</sub>, (l) BaS, (m) O<sub>2</sub>.
23. There are three possible positions for hydrogen in the Periodic Table:
  - (a) above lithium, (b) above fluorine, (c) above and a little to the left of carbon. Explain the respective merits of each position.
24. In the table of simple and complex ions (Table 7.15)
  - a. Memorize all ions: name, formula and charge.
  - b. Write the total electronic configuration of all ions checked (✓).
  - c. Write the valence electron structure (dot formula) for all starred (\*) ions.
  - d. Be able to write the correct formula for the ionic compound that might be formed from each pair of plus and minus ions.
25. Write correct formulas for: (a) aluminum nitrate, (b) sodium phosphate, (c) calcium bicarbonate, (d) silver chromate, (e) nickel sulfate, (f) barium sulfide, (g) potassium bromide, (h) ammonium nitrite, (i) calcium carbonate, (j) mercurous chloride.

## GASES, LIQUIDS AND SOLIDS

The states of matter were discussed briefly and qualitatively in a previous chapter. Now the subject will be discussed more thoroughly and, in the case of gases, quantitatively. It is hoped that the discussion will lay a foundation for an understanding of the molecular theory of matter.

### 1. THE GASEOUS STATE

Everyone is acquainted with gases, especially the gas mixture called air. In many ways a gas mixture behaves like a pure gas. For this reason air can be used as an example in much of our discussion.

It is common knowledge that air can be compressed into a smaller volume. It is also common knowledge that, as it is compressed, it exerts a force (called pressure) resisting that compression. This principle can be illustrated by consideration of an old fashioned tire pump. The pump (Fig. 8.1a), composed of a narrow, hollow metal cylinder about two feet in length and two inches in diameter, is closed at one end. The tube is fitted with an air tight piston that can be raised and lowered by means of a metal rod with a wooden handle. Near the bottom, or closed end, a rubber hose is connected to the cylinder. When in use, the other end of the hose is connected to the valve stem of a tire. Near the top of the cylinder is a small hole or air vent.

In operation, with the hose connected to the tire valve stem, the piston is raised to the top (Fig. 8.1b), admitting air to the cylinder through the air vent. The piston is then forced down, trapping the air in the cylinder and compressing it as the downward motion continues. As the piston approaches the bottom of the tube, the pressure of the air in the cylinder becomes sufficiently great that it is difficult to finish the stroke. When the pressure of the air in



the pump exceeds the pressure in the tire, it is admitted to the inner-tube by the action of a one-way valve. The piston is raised again, admitting more air to be compressed in the cylinder and admitted to the tire. The process is repeated over and over until the tire is inflated. Anyone who has inflated a tire with a pump knows that a large quantity of compressed air must be added. The resulting pressure is sufficient to support an automobile.

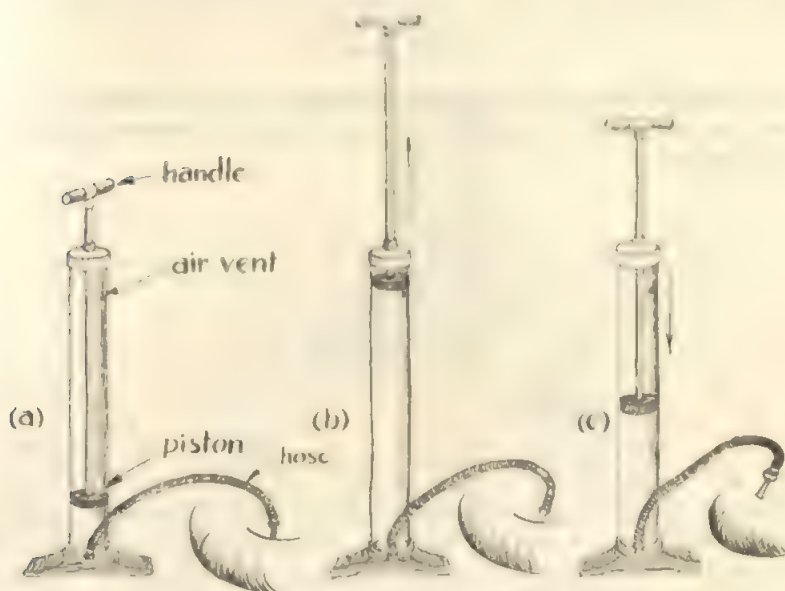


Figure 8.1. Tire pump.

Compressed air keeps a football "tight"; it keeps a deep-sea diver's suit from being crushed with the tons of water over him. It operates jack-hammers, paint sprayers, and many water-pressure systems.

### A. BOYLE'S LAW

The quantitative relationship between the volume and the pressure exerted by a sample of gas is given by Boyle's Law. Robert Boyle (1627-1691), one of the founders of modern science, investigated the matter and came to the conclusion that *when the temperature is maintained constant, the volume of a given sample of gas varies inversely with the pressure.* This means that if the pressure is doubled, the volume of the sample will be halved. It also tells us that if two liters of air at 14.5 pounds per square inch pressure is compressed until the pressure is 43.5 pounds per square inch, the volume will be just 2/3 liters.

$$\text{or } 2 \text{ L} \times \frac{14.5 \text{ lbs/in}^2}{43.5 \text{ lbs/in}^2} = 2/3 \text{ L}$$

The law may be expressed mathematically as follows:

$$V \propto \frac{1}{P}, V = \frac{k}{P} \text{ (where } k \text{ is a constant)}$$

$$\text{or } VP = k \text{ (where } k \text{ is a constant)}$$

But this is true only when the temperature and the amount of gas do not change. If any leakage occurs, the law does not apply.

### B. MANOMETER

In scientific work, pressure is often expressed in “mm of mercury” because a mercury manometer, which is often used to measure pressure, can be read in millimeters.

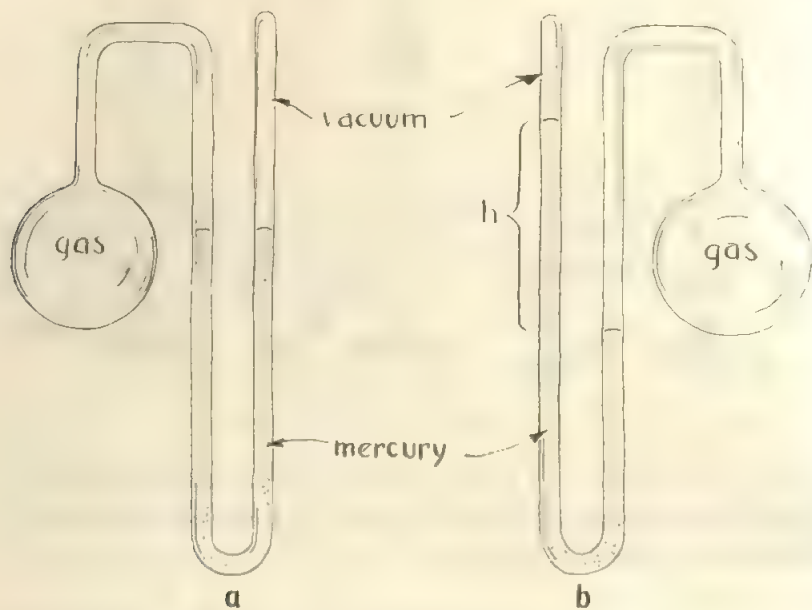


Figure 8.2. Closed-end manometer.

The closed-end manometer (shown connected to a glass bulb in Figure 8.2) is a slender U-tube, mounted vertically with mercury filling the lower portion. One arm of the U-tube is sealed off. Before sealing, the air was pumped from it, leaving it as nearly a complete vacuum as possible. The other arm is connected to a container holding a gas sample.

Figure 8.2a shows the position of the mercury when the gas bulb contains no gas. No gas pressure acts on either mercury surface, so they are level. In Figure 8.2b, a sample of gas has been admitted to the bulb. The pressure in the flask has pushed the mercury down and up into the closed arm of the U-tube. The pressure is proportional to the height ( $h$ ) that the mercury level rises in the closed arm of the manometer above the level in the other arm.

One may calculate the pressure in the usual units of pounds per square inch from the density and height of the mercury, but it shall not be done here. The pressure is read as the difference in millimeters between the two levels.

A barometer is a special type of closed-end manometer used to measure the pressure of the gaseous atmosphere around us. The earth is surrounded by a layer of air some 50 miles in depth. The air layer is pulled to the earth by gravity and therefore presses down upon all objects on its surface.

One can observe the effects of atmospheric pressure by attaching a vacuum pump to an empty can. As the air is pumped out and the pressure inside



Figure 8.3. Drawing liquid through a straw.

decreases, the weight of the atmosphere crushes it. Atmospheric pressure is also observed when one drinks a beverage through a straw. One doesn't draw the liquid up the straw, but he draws air out of the straw, decreasing the pressure. The air around the straw and above the liquid pushes it down and up through the straw (Fig. 8.3).

The barometer may be a simple, closed-end manometer open to the air (Fig. 8.4a), but usually it is a straight, closed-end vacuum tube in a dish of mercury (Fig. 8.4b). Both types operate on the same principle. The air pushes down on the open surface, forcing the mercury column up the tube until its weight per square centimeter is equal to the atmospheric pressure.

The earth's surface is uneven, with low valleys, high land and mountain ranges penetrating the atmosphere. At higher elevations the air blanket is not so thick and the atmospheric pressure is less than at sea level. At sea level the average barometric pressure is 760 mm or 14.7 pounds per square inch. This value has been taken as a standard for comparing gases. When one speaks of a gas at *standard pressure*, he means a *pressure of 760 mm of mercury*. This is the unit of pressure in another scale. One atmosphere (1 atm) is 760 mm;  $2 \text{ atm} = 2 \times 760 \text{ mm} = 1520 \text{ mm}$ . At higher elevations the barometric pressure averages about 640 mm or 640/760 of one atmosphere.

The barometer is used in weather forecasting. When the humidity (relative moisture content) of the air is high, water vapor takes the place of the heavier air, the pressure decreases and the barometer drops. Should the mass of moisture-laden air contact a similar mass of cold air, rain or snow results.

Open-end manometers are sometimes used to measure gas pressures. One, attached to a gas bulb, is sketched in Figure 8.5. In Figure 8.5a, the mercury levels are the same, and the pressure on the gas sample is equal to the barometric pressure (assumed to be 640 mm) since the barometric

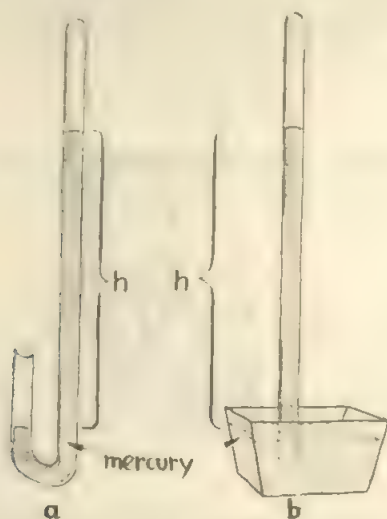


Figure 8.4. Barometers.

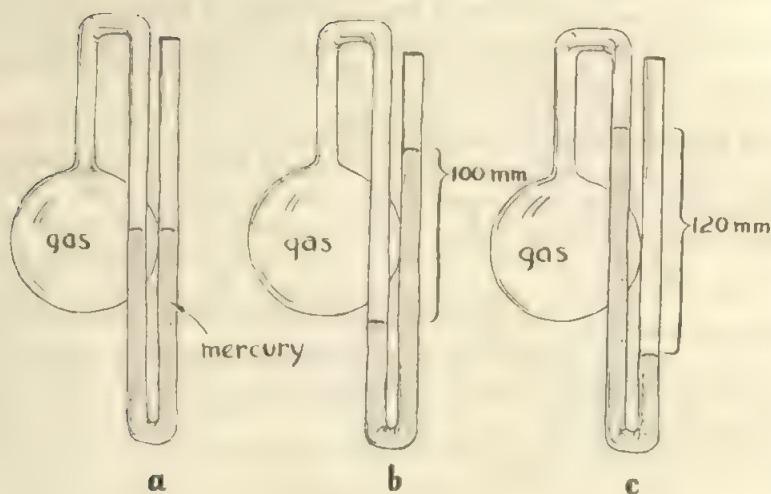


Figure 8.5. Open-end manometer.

pressure acts on the surface open to the atmosphere. In Figure 8.5b, the pressure on the gas sample = barometric + 100 mm = 640 mm + 100 mm = 740 mm. In Figure 8.5c the pressure exerted on the gas sample is less than barometric pressure = (640 - 120) mm = 520 mm.



Calculations of change in gas volume with pressure when the pressure is stated in "mm mercury" are similar to those with the pressure given in pounds per square inch.

**EXAMPLE 1.** 150 ml of hydrogen gas at 25°C and 760 mm is expanded until the pressure is 380 mm. Calculate the final volume.

**SOLUTION.** The volume varies inversely with the pressure. Here the pressure is reduced from 760 mm to 380 mm, and the volume increases by the factor 760/380.

$$150 \text{ ml} \times \frac{760 \text{ mm}}{380 \text{ mm}} = 300 \text{ ml}$$

(One may note that the label on the answer is correct; milliliters expresses volume.)

**EXAMPLE 2.** Find the volume at standard pressure and 18°C of a 2.5 L air sample measured at 18°C and 570 mm.

**SOLUTION:** As the pressure increases, the volume decreases. The decrease is given by the ratio of the pressures.

$$2.5 \text{ L} \times \frac{570 \text{ mm}}{760 \text{ mm}} = 1.87 \text{ L}$$

The pressures may be stated in atmospheres (Example 3).

**EXAMPLE 3.** 280 ml of oxygen gas at 25°C and 1 atm is compressed to 1.5 atm at the same temperature. Find its final volume.

$$280 \text{ ml} \times \frac{1 \text{ atm}}{1.5 \text{ atm}} = 186 \text{ ml}$$

### C. BOYLE'S LAW APPARATUS

A simple laboratory apparatus for examining Boyle's Law is shown in Figure 8.6a. A sample of air is trapped in the inverted tube by mercury which fills the lower end of the tube, a connecting hose and a leveling bulb. The inverted tube acts both as the gas container and one arm of the manometer. The leveling bulb and hose are the other arm and are also a device for varying the pressure on the gas sample. When the leveling bulb is raised, mercury runs into the tube, compressing the sample. The pressure on the sample at any instant is equal to the barometric pressure plus the difference in mercury levels if the bulb is above, or the barometric pressure minus the difference in levels if the bulb is below. The length of the gas sample (that is, the distance from the end of the closed tube to the mercury level) is a measure of the volume.

Suppose that at a barometric pressure of 640 mm the leveling bulb is adjusted so that the level of the mercury in it is 140 mm below the level in the tube (Fig. 8.6b) and the length of the gas sample is 250 mm at 25°C. Now,

with no change in temperature and no leakage, the leveling bulb is lifted until the level of mercury in it is 110 mm above the level in the tube (Fig. 8.6c).

If Boyle's Law obtains, the new volume may be calculated this way:

250 "mm" volume at  $(640 - 140)$  mm pressure and  $25^{\circ}\text{C}$  is compressed to a pressure of  $(640 + 110)$  mm. What is the resultant volume?

$$250 \text{ "mm"} \times \frac{500 \text{ mm}}{750 \text{ mm}} = 167 \text{ "mm"}$$

The measurement shows that the air sample is 167 mm, as shown in Figure 8.6c. Boyle's Law is verified.

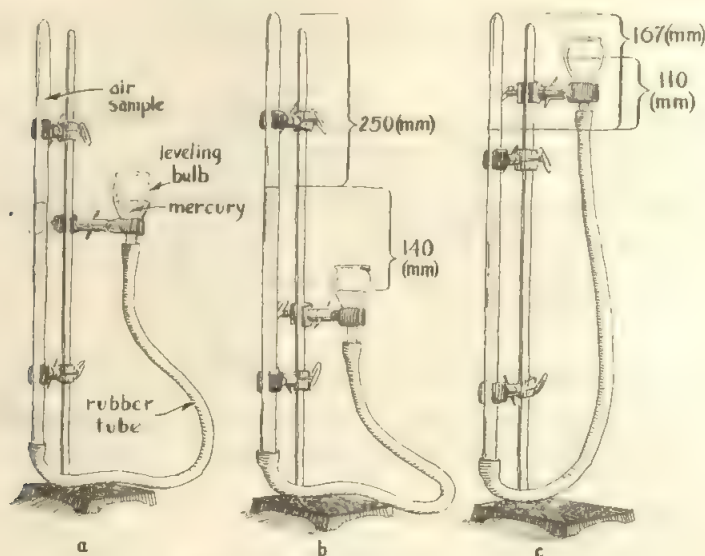


Figure 8.6. Boyle's law apparatus.

#### D. TEMPERATURE

The next gas law is concerned with the variation of volume with temperature changes. This requires a definition or discussion of temperature. Some qualitative statements of temperatures are: "It is hot." "It is warm." "It is cold." When a person says, "The beaker is hot," he means that the beaker is of such a temperature that when in contact with his hand or skin, heat flows from it to his hand, giving a burning sensation.

The first law of temperature states that when two objects are brought in contact, heat must flow from the one of higher temperature to the other. Our skin is sensitive to heat flow so that one can touch an object and sense that its temperature is higher, lower, or the same as body temperature. It is difficult, however, to tell by the sense of touch, *how much* colder one object is than another. A good conductor, such as iron, copper, or another metal, feels colder than the rug or straw it lies upon, because it carries the heat away faster. Thus, the sensation of heat flow is not a suitable standard for measuring temperature.

For centuries it has been known that most substances expand on heating and contract on cooling. Furthermore, with liquids and solids, on which ordinary pressure changes have little effect, the volume is always the same at the same temperature. The volume then if calibrated can be a quantitative measure of the temperature of the object or material that surrounds it. Ordinary thermometers operate upon that principle, measuring the temperature by the extent of expansion of a liquid.

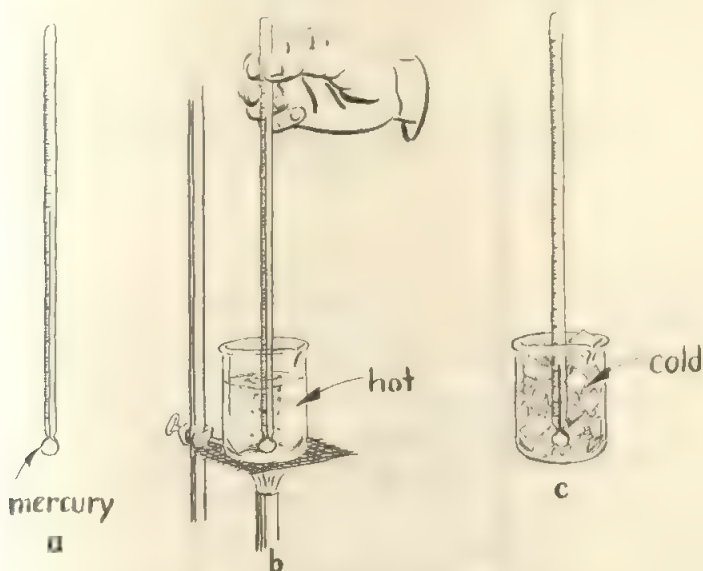


Figure 8.7. Mercury thermometer.

The *mercury thermometer* utilizes the thermal expansion of mercury to indicate temperature. The expansion of mercury with small temperature changes is so slight as to be unobservable if the mercury is contained in an ordinary container. The thermometer is simply a glass bulb sealed to a fine capillary tube and filled with mercury such that it stands part way up the capillary (Fig. 8.7a).

Expansion of the mercury appears as a rising thread in the capillary tube. The thread rises when the mercury is heated and shrinks back when it is cooled. Graduations appear on the capillary tube or on a card mounted adjacent to it where one can read the temperature directly. Two temperature scales are used: the Fahrenheit and the centigrade. Thermometers are known by the scale they carry.

Zero on the *Fahrenheit thermometer* was set by placing an unmarked thermometer in the coldest mixture of ice, water and salt that could be made. The position of the mercury was marked on the glass and labeled  $0^{\circ}\text{F}$ . This temperature was assumed to be the lowest temperature to be often attained. Body temperature was then selected to be 100. The thermometer was placed in someone's mouth and the mercury level marked and labeled  $100^{\circ}\text{F}$ . It is

interesting that normal body temperature was measured incorrectly by 1.4°. To finish the thermometer, the distance between the 0° and 100° marks was divided into 100 equal portions with 99 marks. Degrees of the same length are marked off above 100° and below 0° to complete the scale (Fig. 8.8). With this thermometer, the freezing point of water is +32° and the boiling point is 212°. There are 180° between the freezing and the boiling points of water. This is the scale used commonly by doctors, weather observers, cooks and most industrial establishments.

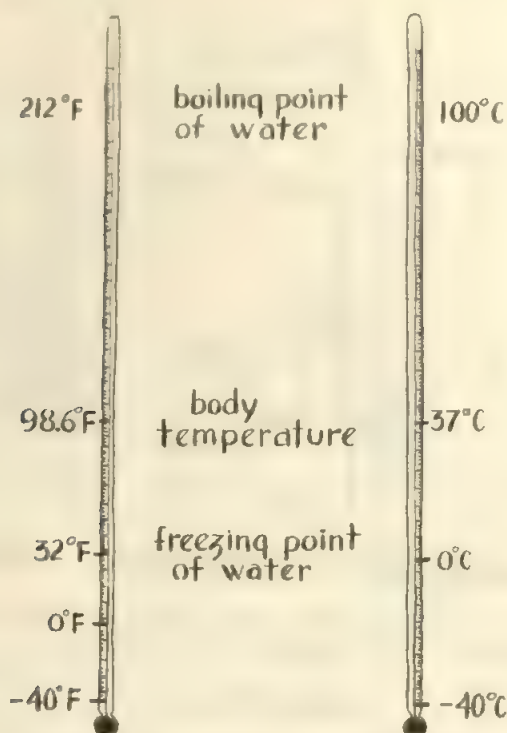


Figure 8.8. Fahrenheit and centigrade scales.

Physical properties of water are standards for the centigrade thermometer. The freezing point of pure water is taken as zero, the boiling point at 760 mm as 100°C. To calibrate the thermometer, one merely places it in a slush of ice and water, makes a mark on the glass even with the mercury and labels it 0°C. He sets the pressure above a vessel of water at 760 mm, heats the vessel until the water boils, and holds the bulb just above the water until steam condenses on it and drips steadily back into the vessel. He marks the mercury level on the glass and labels it 100°C. As before, the thermometer between 0° and 100° is divided into 100 equal portions. Degrees of equal length are marked above 100°C and below 0°C as with the Fahrenheit thermometer.

The centigrade scale is used in scientific work. It was found to be much easier to calibrate a thermometer with the centigrade scale than with the



Fahrenheit. Normal body temperature varies, and a mixture of ice, salt, and water giving the lowest temperature is difficult to prepare.

Both scales may be placed on the same thermometer. The mercury stands the same place at the same conditions regardless of the scale, but the scales are set in relation to each other so that mercury is: at 32° on the Fahrenheit scale and 0° on the centigrade at freezing; at 98.6° F and 37° C when placed in your mouth; and at 212° F and 100° C in boiling water (Fig. 8.8).

One can convert °F to °C, and vice versa, if he remembers that there are 212° - 32° = 180° F between freezing and boiling, but only 100° - 0° = 100° C. Thus the centigrade degree is  $180/100 = 9/5$  as large as the Fahrenheit degree. 0°C starts at 32°F so:

$$\text{degrees C} = (\text{degrees F} - 32) \times 5/9$$

EXAMPLE. How is 88° F expressed in the centigrade scale?

$$(88 - 32)5/9 = 31.1^{\circ}\text{C}.$$

### E. CHARLES' LAW

When a given quantity of air is heated, it must either increase in volume or pressure or both. This is commonly known. If one has his automobile tires filled to the required pressure in cold weather, he will find on checking his tires after driving for some distance that the pressure has increased several pounds per square inch. He might notice that the tires are hot from the friction on the road surface. When the tires are cooled, the pressure returns to its initial value. Children become victims of this phenomenon when they take air-filled balloons out in the hot sun, only to see them expand and burst. The expansion of air with the heat absorbed at the earth's surface and the attendant decrease in density account for its rising and displacement with cold air from above. A wind is just a large scale displacement of warm, rising air with cold air.

The French physicist, J. A. C. Charles (1746-1823), studied the effect of temperature changes on the volume of a sample of gas at constant pressure. He made observations such as these:

- When a gas sample is heated from 0°C to 1°C, the final volume is  $274/273$  of the initial volume.
- When a gas sample is heated from 25°C to 30°C, the volume increases to  $303/298$  of its original value.

That is, a 250 ml sample of air at 25°C and 1 atm is heated to 30°C at 1 atm. Its final volume is 254 ml

$$\text{and } 250 \text{ ml} \times \frac{303}{298} = 254 \text{ ml}$$

- When a sample of gas is heated from 100°C to 105°C, the volume increases to  $378/373$  of its original value.

That is: 3.40 L of gas at 100°C became

$$3.40 \text{ L} \times \frac{378}{373} = 3.45 \text{ L}$$

As expected, an increase in volume always attended a rise in temperature. Furthermore, if he added 273 to each temperature, then multiplied the original volume by the ratio of the final temperature over the initial temperature, he could calculate the final volume. Notice in the three examples (a, b and c) given above  $274 = 273 + 1^\circ\text{C}$ ,  $273 = 273 + 0^\circ\text{C}$ ,  $303 = 273 + 30^\circ\text{C}$ ,  $298 = 273 + 25^\circ\text{C}$ ,  $378 = 273 + 105^\circ\text{C}$ , etc.

To illustrate, the calculation for Example c is:

$$3.40 \text{ L} \times \frac{273 + 105^\circ\text{C}}{273 + 100^\circ\text{C}} = 3.40 \text{ L} \times \frac{378}{373} = 3.45 \text{ L.}$$

Charles further reasoned that, since the method applied at all temperatures,  $-273^\circ\text{C}$  must be the absolute bottom of temperature and that  $25^\circ\text{C}$  was really  $273 + 25 = 298$  above the bottom or lowest possible temperature. Readings on this new temperature scale are then *absolute*.

$$25^\circ\text{C} = 273 + 25^\circ\text{absolute} = 298^\circ\text{A}$$

$$-60^\circ\text{C} = (273 - 60)^\circ\text{A} = 213^\circ\text{A}$$

In all cases, 273 is added to the temperature in  $^\circ\text{C}$  to find  $^\circ\text{A}$ . A simple conversion of  $^\circ\text{C}$  to  $^\circ\text{F}$  shows that  $0^\circ\text{A}$  is also  $-459^\circ\text{F}$ . The three temperature scales are compared in Table 8.1. The Absolute Temperature Scale used here is identical with the Kelvin Temperature Scale and in every case  $^\circ\text{K}$  can be substituted for  $^\circ\text{A}$ .

**Table 8.1. Fahrenheit, Centigrade and Absolute Temperature Scales**

392 $^\circ\text{F}$ —	200 $^\circ\text{C}$ —	473 $^\circ\text{A}$
212 $^\circ\text{F}$ —	100 $^\circ\text{C}$ —	373 $^\circ\text{A}$
32 $^\circ\text{F}$ —	0 $^\circ\text{C}$ —	273 $^\circ\text{A}$
-148 $^\circ\text{F}$ —	-100 $^\circ\text{C}$ —	173 $^\circ\text{A}$
-328 $^\circ\text{F}$ —	-200 $^\circ\text{C}$ —	73 $^\circ\text{A}$
-459 $^\circ\text{F}$ —	-273 $^\circ\text{C}$ —	0 $^\circ\text{A}$

It is of interest that further research has shown Charles to be correct.  $-273^\circ\text{C}$  (or more exactly,  $-273.16^\circ\text{C}$ ) is the lowest temperature possible. Thermodynamic studies verify it. Zero degrees absolute has almost been attained in the laboratory, that is, within a few thousandths of a degree.

The formal statement of Charles' Law is then apparent: "*With the pressure constant, the volume of a sample of gas varies directly with the absolute temperature.*" This law may be stated mathematically:

$$V \propto T, \quad V = kT \quad \text{or} \quad V/T = k$$

(where  $k$  is a constant)

$$\text{or} \quad \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

where  $V_1$  and  $T_1$  equal the volume and temperature respectively at one time. And  $V_2$  and  $T_2$  are the volume and temperature of the same gas sample at another volume and temperature. It must be stressed that the law holds only when gas is neither added to nor lost from the sample, and when the pressure remains constant.

In solving problems using Charles' Law, one might substitute into various forms of the equations above or he might apply the corrections to the volume as Charles found them.

**EXAMPLE 1.** A 150 ml sample of oxygen at 1 atm and 25 °C is heated to 80 °C, with the pressure remaining at 1 atm. Calculate the final volume

$$150 \text{ ml} \times \frac{(273 + 80)^{\circ}\text{A}}{(273 + 25)^{\circ}\text{A}} = 177 \text{ ml}$$

Reasoning it through, one would first change all temperatures to °A. He would say to himself, "The temperature is raised from 298°A to 353°A." The volume increases with a rise in temperature, so multiply the volume by a fraction of the temperatures greater than 1, that is 353/298 and not 298/353. The answer is a larger final volume (177 ml) than the original (150 ml), as anticipated.

**EXAMPLE 2.** 3.5 L of nitrogen at -23 °C is heated to 210 °C. During the process the pressure remains at 640 mm. To what volume did the nitrogen expand?

The temperatures are

$$273 - 23^{\circ}\text{C} = 250^{\circ}\text{A} \quad \text{and}$$

$$273 + 210 = 483^{\circ}\text{A}$$

The volume increases with the temperature:

$$3.5 \text{ L} \times \frac{483^{\circ}\text{A}}{250^{\circ}\text{A}} = 6.75 \text{ L}$$

A *standard temperature* has been chosen to be used with *standard pressure* when gas volumes are compared. Standard temperature is 0°C or 273°A.

**EXAMPLE 3.** What is the volume at STP (Standard Temperature and Pressure) of 2.60 L of oxygen measured at 760 mm and -27 °C?

**SOLUTION:** The temperature decreases by the fraction:

$$\frac{273}{273 + 27} \quad \frac{273^{\circ}\text{A}}{300^{\circ}\text{A}}$$

and so does the volume:

$$2.60 \text{ L} \times \frac{273^{\circ}\text{A}}{300^{\circ}\text{A}} = 2.34 \text{ L}$$

#### F. CHARLES' LAW APPARATUS

With additional equipment the apparatus used to test Boyle's Law (Fig. 8.6) may be used to study Charles' Law. This addition is a glass jacket around the sample tube connected through a rubber tube to an Erlenmeyer flask partly filled with water and arranged so that it may be heated at the proper time (Fig. 8.9).

Again the volume of the air sample trapped in the closed-end tube is

proportional to the length of the tube it occupies. The pressure is equal to the barometric pressure plus the vertical distance from the mercury level in the bulb to the level of that liquid in the sample tube.

To test Charles' Law, one may measure the "volume" (length) of the sample and the vertical distance between the mercury levels at room temperature, recording both of these measurements along with the temperature.

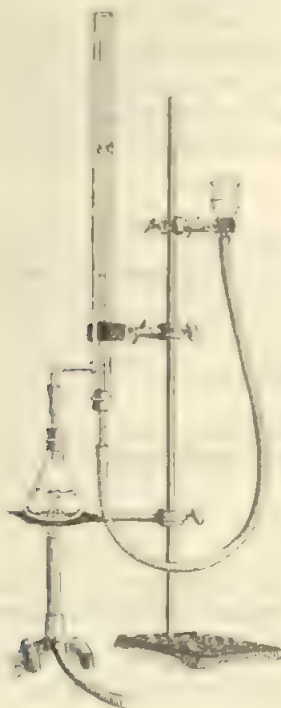


Figure 8.9. Charles' law apparatus.

Next the water in the flask is boiled gently until steam rises in the jacket and envelopes the tube containing the air sample, raising it to the boiling point of water at the prevailing atmospheric pressure. The gas sample expands, which also changes the vertical distance between the mercury levels. The leveling bulb must then be lowered until the same difference exists between the mercury levels as it did at room temperature. The new volume (length) of the sample is then measured. One may calculate the new volume at boiling temperature from the volume measured at room temperature by Charles' Law and see how closely it agrees with the measured volume.

A sample calculation is shown below. Suppose the "length" of the air sample is 180 mm at  $23^{\circ}\text{C}$ , room temperature, with the barometric pressure at 630 mm and the mercury level in the bulb 90 mm above the level in the sample tube. What should the volume (length) be when surrounded with steam with the mercury levels again adjusted to a vertical distance of 90 mm?



**SOLUTION:** *Initially* there are 180 "mm" of air in the tube at 23°C (296°A) and 630 mm  $\rightarrow$  90 mm = 720 mm. Finally, the sample is at 720 mm as before and at 95°C (368°A), the boiling point of water when the barometric pressure is 630 mm. The "length" should increase by the factor 368 A/296°A and is then:

$$180 \text{ "mm"} \times \frac{368^{\circ}\text{A}}{296^{\circ}\text{A}} = 224 \text{ "mm"}$$

Because temperature and pressure have an independent effect on volume changes, one can carry out corrections for both on the same sample of gas and may do so in either order.

**EXAMPLE 1.** Find the volume at STP of 180 ml of nitrogen measured at 35°C and 540 mm.

*Initially:* 180 ml at (35°C + 273)°A and 540 mm

*Finally:* ? ml at 273°A and 760 mm

The volume decreases with the temperature:

$$180 \text{ ml} \times \frac{273^{\circ}\text{A}}{308^{\circ}\text{A}}$$

and decreases when the pressure increases:

$$180 \text{ ml} \times \frac{273^{\circ}\text{A}}{308^{\circ}\text{A}} \times \frac{540 \text{ mm}}{760 \text{ mm}} = 113 \text{ ml}$$

**EXAMPLE 2.** What volume will 265 ml of a gas at -23°C and 1520 mm occupy at 640 mm and 0°C?

*Initially:* 265 ml at (273 - 23)°A and 1520 mm

*Finally:* ? ml at 273°A and 640 mm

The volume increases as the temperature increases:

$$265 \text{ ml} \times \frac{273^{\circ}\text{A}}{250^{\circ}\text{A}}$$

and increases as the pressure decreases:

$$265 \text{ ml} \times \frac{273^{\circ}\text{A}}{250^{\circ}\text{A}} \times \frac{1520 \text{ mm}}{640 \text{ mm}} = 687 \text{ ml}$$

**EXAMPLE 3.** What is the volume at STP of 1.54 L of oxygen at 2.4 atm and 90°C?

*Initially:* 1.54 L at 2.4 atm and (90 + 273)°A

*Finally:* ? L at 1.0 atm and 273°A

$$1.54 \text{ L} \times \frac{2.4 \text{ atm}}{1 \text{ atm}} \times \frac{273^{\circ}\text{A}}{363^{\circ}\text{A}} = 2.78 \text{ L}$$

### G. DALTON'S LAW OF PARTIAL PRESSURES

The third of the quantitative laws describing the behavior of gases was formulated by John Dalton (1766-1844), the same Dalton whose atomic

theory has been discussed. He found from his experience with air and other gas mixtures that *in a mixture of gases, the total pressure exerted by the mixture is equal to the sum of the pressure each gas would exert if alone in the container.* This concerns a mixture and not a compound formed by the combination of the gases when mixed.

Individual gases of a mixture diffuse through each other and throughout the entire volume of the container. In that sense each gas fills the container, but in so doing, its contribution to the total pressure is only that which it would exert if alone in the container. The total pressure is then the sum of the pressures of each gas in the mixture. Gases in a mixture do not divide the volume among themselves but divide the pressure.

Some calculations using Dalton's Law are shown below:

**EXAMPLE 1.** In a mixture of nitrogen and hydrogen gases with a total pressure of 760 mm mercury, nitrogen exerts a pressure (partial pressure) of 190 mm. Find the pressure of hydrogen in the mixture.

**SOLUTION:** The total pressure = pressure of nitrogen + pressure of hydrogen

$$P_T = P_{N_2} + P_{H_2}$$

$$\text{and } P_{H_2} = P_T - P_{N_2}$$

$$= 760 \text{ mm} - 190 \text{ mm} = 570 \text{ mm}$$

**EXAMPLE 2.** 100 ml of oxygen at 380 mm and 25°C is placed in a 200 ml flask. Carbon dioxide is added to the flask with the oxygen until the total pressure is 640 mm. Calculate the pressure of (a) oxygen and of (b) carbon dioxide in the flask.

**SOLUTION:** a. If no  $\text{CO}_2$  were present, a "Boyle's Law" calculation would tell us:

$$P_{O_2} = 380 \text{ mm} \times \frac{100 \text{ ml}}{200 \text{ ml}} = 190 \text{ mm}$$

Furthermore, addition of  $\text{CO}_2$  does not alter the pressure exerted by oxygen; it remains 190 mm.

b. The carbon dioxide exerts the balance of the 640 mm:

$$P_{\text{CO}_2} = 640 \text{ mm} - 190 \text{ mm} = 450 \text{ mm}$$

**EXAMPLE 3.** How many ml of oxygen gas measured at 760 mm and 20°C must be added to 500 ml of neon at 460 mm and 20°C to bring the total pressure to 760 mm?

**SOLUTION:** The pressure of oxygen in the mixture in a 500 ml container must be:  $760 \text{ mm} - 460 \text{ mm} = 300 \text{ mm}$ .

That is, 500 ml at 300 mm are needed. At 760 mm the volume will be:

$$500 \text{ ml} \times \frac{300 \text{ mm}}{760 \text{ mm}} = 197 \text{ ml}$$

**EXAMPLE 4.** 400 ml of oxygen and 100 ml of nitrogen both at STP are allowed to mix in a larger volume at a total pressure of 640 mm, the temperature remaining at 0°C.

(a) What is the partial pressure of oxygen? (b) What is the volume of the container?

**SOLUTION:** a. 4/5 of the gas by volume is oxygen. It will exert 4/5 of the final pressure.

$$\begin{aligned} & \frac{400 \text{ ml}}{(100 \text{ ml} + 400 \text{ ml})} \times 640 \text{ mm} \\ &= \frac{400 \text{ ml}}{500 \text{ ml}} \times 640 \text{ mm} = 4/5 \times 640 \text{ mm} = 512 \text{ mm} \end{aligned}$$

b. The oxygen pressure in the new container is 512 mm (part a). 400 ml of oxygen at 760 mm and 0°C is changed to 512 mm and 0°C. Its volume is then:

$$400 \text{ ml} \times \frac{760 \text{ mm}}{512 \text{ mm}} = 594 \text{ ml}$$

594 ml is the total volume, for all gases in a mixture occupy the total volume and divide the pressure among themselves.

It should be noted in passing that Charles', Boyle's and Dalton's Laws do not hold precisely. That is, when one calculates a new volume of a gas sample with changes in temperature or pressure, or both, and then measures very precisely, he will find a small error. The error varies with the kind and conditions of the gas. However, if the initial and final temperatures are well above the condensation temperature of the gas (the boiling point of its liquid), and if the pressures are no more than a few atmospheres, the error is usually small enough to be neglected.

The nature of the error and its source will be discussed in part in the next chapter.

## 2. THE LIQUID STATE

Under the proper conditions any and all gases may be liquefied. Water vapor, a gas, may be liquefied by holding a cold spoon over the spout of a boiling kettle. Rain occurs as a result of such a condensation of water vapor. The reverse process, the change of a liquid to a gas, has often been observed. Boiling water decreases in amount as it evaporates. Even at room temperature water evaporates slowly. The liquids, alcohol, acetone, gasoline and ether evaporate more readily at room temperature.

### A. VAPOR PRESSURE

A careful study of the phenomenon of evaporation is interesting. Consider a container partially filled with water, attached to a manometer, from which the air has just been pumped. At the instant the apparatus is isolated from the pump (by closing the stopcock), the mercury levels in the manometer are

Table 8.2. Vapor Pressure Table for Water

Temperature °C	Pressure mm	Temperature °C	Pressure mm
0	4.6	50	92.5
5	6.5	60	149.4
10	9.2	70	233.7
15	12.8	80	355.1
20	17.5	90	525.8
25	23.8	100	760.0
30	31.8	110	1074.6
35	42.2		
40	55.3		

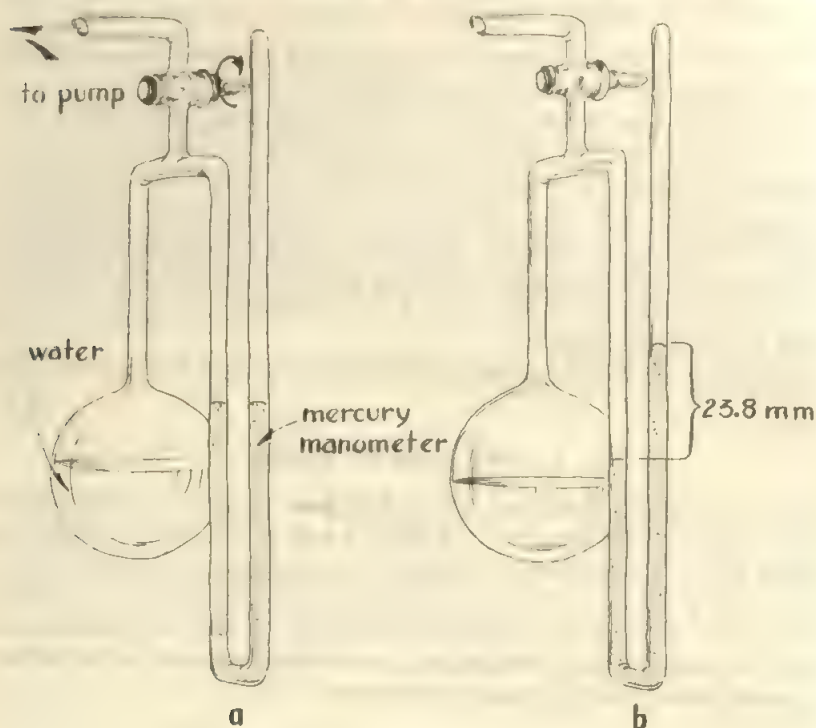


Figure 8.10. Vapor pressure apparatus.

level, as shown in Figure 8.10a. However, evaporation rapidly occurs and vapor pressure above the liquid rises rapidly, pushing the mercury level down and up into the closed end of the manometer. Very shortly the pressure ceases changing and the levels in the mercury manometer remain constant unless the temperature changes. At 25°C the difference in the mercury levels,



the pressure, is 23.8 mm (Fig. 8.10b). This is called "the vapor pressure" of water at 25°C.

This vapor pressure of water can be changed in only one way—by changing the temperature. Neither adding more liquid nor admitting gas above the liquid has any measurable effect on the vapor pressure of water. If the temperature is lowered, the vapor pressure decreases; if it is raised, the vapor pressure increases. The vapor pressures of water at various temperatures are listed in Table 8.2.

### B. BOILING POINT

At standard pressure, water boils at 100°C. At this temperature, bubbles appear in the water, rising to the top and bursting, violently agitating the entire liquid. Under these conditions, the water disappears very rapidly. At all temperatures below 100°C, water cannot boil when the atmospheric pressure is 760 mm, and the loss of water to vapor is relatively slow. When the vapor pressure reaches 760 mm, gas bubbles can grow in the liquid because the pressure in the vapor sphere is greater than the pressure that rests down upon it. At this point, molecules are not only escaping from the surface, but are escaping into the bubbles of vapor which grow very rapidly as they rise to escape. Vapor escapes so rapidly, absorbing heat of vaporization, that the temperature of the liquid at the surface never rises above 100°C.

At higher altitudes water boils at about 95°C, because the average barometric pressure is about 645 mm. A vapor pressure of 645 mm corresponds to a temperature of 95°C. Of course, the vapor pressure of water does not terminate at 760 mm, but rises beyond at higher temperatures in a closed container. A pressure cooker uses this principle. Water vapor is retained to give a higher pressure. At a gauge pressure of 5 lb per square inch, an additional pressure of about 250 mm, the temperature is 108°C. The rate of chemical reactions, among which are cooking reactions, is often doubled by an increase in temperature of 10°C. Therefore, cooking can be speeded very greatly by the higher temperature of reaction.

### C. VAPOR PRESSURE IN GASES

Water evaporates from lakes and rivers into the atmosphere continuously, that is, until the humidity is 100 per cent. When humidity is 100 per cent, the partial pressure of water vapor in the air is the vapor pressure. At 25°C the humidity is 100 per cent when the water vapor in the air has a pressure of 23.8 mm. This is the maximum. At 0°C, 100 per cent humidity is reached at 4.6 mm. This explains why rain or snow occurs when air with a relatively high humidity is cooled suddenly. If air having a humidity of 75% at 25°C (a partial pressure of water vapor of  $.75 \times 23.8 \text{ mm} = 17.4 \text{ mm}$ ) is cooled to 0°C where the vapor pressure, the maximum possible partial pressure of water vapor, is 4.6 mm, the excess water vapor must condense into droplets and fall.

Since gases prepared in the laboratory are often collected over water, a problem arises. Water vapor is contained in the gas, hence the total pressure exerted is not due only to the gas collected. Fortunately, when a sample of gas is confined in a small container with water, the vapor pressure is reached in a moment or two and one may consider the humidity to be 100 per cent. The pressure of the water vapor is then the vapor pressure and may be found in the vapor pressure table (p. 104).

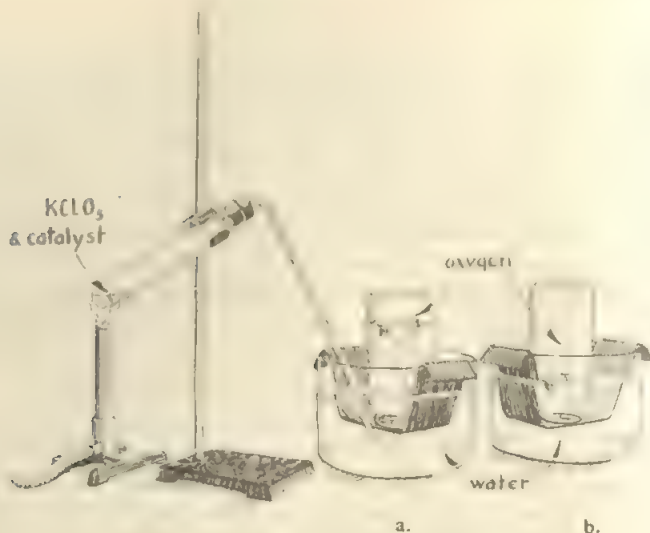
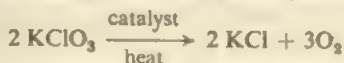


Figure 8.11. Collecting oxygen over water.

Consider an experiment where oxygen is prepared by heating potassium chlorate in the presence of a catalyst in a test tube.



The oxygen is collected by displacement of water from an inverted bottle in a water bath (Fig. 8.11a). As the oxygen is produced and bubbles up through the water in the bottle, the level descends until no more oxygen is produced. To calculate the volume of oxygen at STP, which is often necessary, one must know the pressure in "the mixture," a mixture because it contains water vapor.

To do this, the delivery tube is lowered and removed. The bottle is then adjusted by raising or lowering until the water level inside is level with that in the pan around it (Fig. 8.11b). The pressure of the mixture is then the barometric pressure, in this case, 640 mm. At 20°C the vapor pressure of water (Table 8.2) is 17.5 mm. Applying Dalton's Law, the pressure of oxygen is:

$$\begin{aligned} P_{\text{O}_2} &= P_T - P_{\text{H}_2\text{O}} \\ &= 640 \text{ mm} - 17.5 \text{ mm} \\ &= 622.5 \text{ mm} \end{aligned}$$

**EXAMPLE 1.** What is the pressure of nitrogen which has been collected over water at 25°C and 638 mm?

**SOLUTION:** The vapor pressure of water at 25°C is 23.8 mm (Table 8.2). The partial pressure of nitrogen is:

$$P_{N_2} = 638.0 - 23.8 \text{ mm} = 614.2 \text{ mm}$$

**EXAMPLE 2.** Find the dry volume at STP of 500 ml of nitrogen measured over water at 15°C and 680 mm.

**SOLUTION:**  $P_{N_2} = 680 \text{ mm} - 12.8 = 667 \text{ mm}$ . Applying pressure and temperature corrections to the volume:

$$500 \text{ ml} \times \frac{667 \text{ mm}}{760 \text{ mm}} \times \frac{273^\circ\text{A}}{288^\circ\text{A}} = 416 \text{ ml}$$

**EXAMPLE 3.** What is the dry volume at STP of the oxygen in 400 ml of a mixture of nitrogen and oxygen (80 per cent nitrogen and 20 per cent oxygen by volume) measured over water at 30°C and 720 mm?

**SOLUTION:** The vapor pressure of water at 30°C is 31.8 mm

$$P_{N_2} + P_{O_2} = 720 \text{ mm} - 31.8 \text{ mm} = 688.2 \text{ mm}$$

$$P_{O_2} = 0.20 \times 688 \text{ mm} = 137.6 \text{ mm}$$

In the gas mixture there is 400 ml of oxygen at 30°C and 137.7 mm. At STP the volume would be:

$$400 \text{ ml} \times \frac{137.7 \text{ mm}}{760 \text{ mm}} \times \frac{273^\circ\text{A}}{(273 + 30)^\circ\text{A}} = 65.3 \text{ ml}$$

#### D. SURFACE TENSION

Liquids exhibit a property called surface tension. This property is demonstrated by water spilled on a waxy or oily surface (Fig. 8.12a). Drops of water tend to pull themselves together in a spherical shape as if an invisible membrane held them together. On the other hand, a drop of water spreads out on a *clean*, smooth glass plate in a thin unbroken film (Fig. 8.12b). Again the thin film of water acts like a membrane. Both phenomena are manifestations of surface tension. Water is not attracted to (is incompatible with) wax and pulls itself together. Water is attracted to a clean glass surface. The drop spreads out clinging to as much of the attracting surface as it can. But due to surface tension, the water film remains unbroken; the water holds together. Obviously water molecules exhibit cohesion (attraction for one another).

The rising of a thread of liquid in a glass capillary tube placed in the liquid (Fig. 8.12c) is also due to surface tension. A water film rises up the inside surface of the tube and pulls more liquid up behind it. This results merely in a "rounding up" of the liquid surface at a plane glass surface or inside a large tube, but in a small capillary, the water is pulled from all sides and rises up the tube. The smaller the diameter, the greater the "capillary rise." This

phenomenon accounts in part for the lifting of water from roots to leaves in plants and trees. The water "wets" the inside surface of the capillary tube and pulls the water level with it.

Surface tension varies from substance to substance and decreases with temperature, disappearing at the critical temperature where gas and liquid become identical.

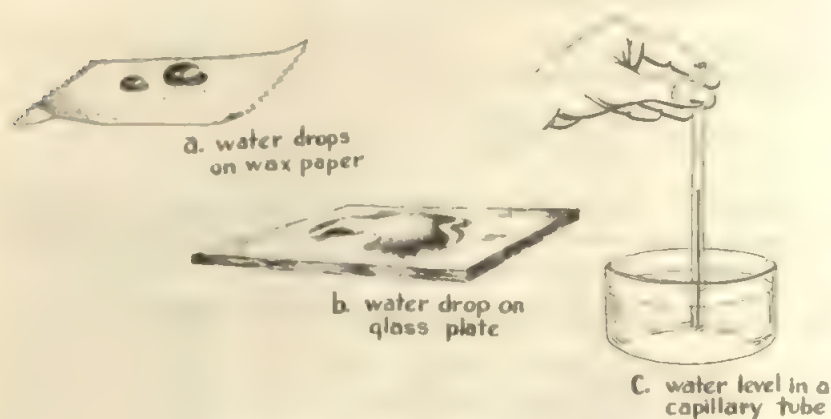


Figure 8.12. Surface tension of water.

### E. VISCOSITY

Another physical property of a liquid is its viscosity, its resistance to flow. Some liquids: (water, gasoline, acetone and cleaning fluid) have a very low viscosity. Others (lubricating oil, honey, tar and phosphoric acid) are very viscous. Viscosity generally decreases with a rise in temperature. For this reason heavier weight lubricating oil can be used in an automobile in the summertime. Some liquids, however, do increase in viscosity when heated.

### F. DIFFUSION AND THE BROWNIAN MOVEMENT

Two additional phenomena, *diffusion* and *Brownian movement*, merit discussion. Diffusion cannot be observed in pure liquids nor in any other homogeneous body of matter. Diffusion can be observed when something is added to change the appearance of a liquid. For example, when a crystal of copper sulfate is placed in a beaker of water, it begins to dissolve, imparting a blue color to the water about the crystal. The color is not confined to the water immediately about the crystal, but it spreads (diffuses) slowly until all the liquid is blue.

The second interesting phenomenon is observed when increasingly small clay particles are dropped into a column of water. At first the heavy particles drop straight to the bottom of the vessel. As the particles become smaller, they fall more slowly until eventually very tiny particles seem to stay suspended



in the water indefinitely. If one observes a single suspended particle with a microscope, he will see that it is zigzagging rapidly in the water, never coming to rest. The phenomenon is well known, it is called the Brownian movement. The path of a particle might be as represented in Figure 8.13.



Figure 8.13. Path of a particle in Brownian movement.

### 3. THE SOLID STATE

Certain aspects of solids have been discussed briefly in two previous chapters. In Chapter 3 outward appearance and the differentiation between a true solid and a plastic or a glass were noted. These are important and shall be discussed here. In Chapter 7 the solid, NaCl (salt), was discussed in relation to its internal bonding. This should be remembered.

#### A. CRYSTAL STRUCTURE

A true solid, as defined by the chemist, must be a pure substance and must exhibit a characteristic crystal pattern. The crystal pattern of a particular

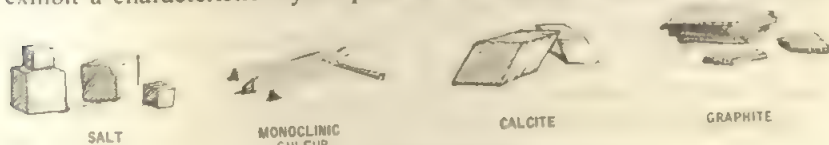


Figure 8.14. Crystals of some pure substances.

solid is often identified by the angles which the faces (flat sides) of the crystal make with one another. The faces of a salt crystal (Fig. 8.14) are perpendicular to one another, and the crystals appear as cubes or rectangular boxes. Adjacent faces of calcite crystals are not perpendicular to one another, but opposite faces are parallel. Graphite crystals are thin platelets. Each true solid has its own crystal pattern and every crystal of the solid conforms to the pattern (Fig. 8.14).

## B. MELTING POINT

A true solid has a definite and constant melting point (melting temperature). Each sample of a true solid begins to melt at that temperature and remains at that temperature until completely melted. In contrast pseudo-solids soften over a range of temperatures. This property can be illustrated by an experimental determination of the melting point of ice, a true solid.

A beaker of ice with a thermometer frozen in it is removed from a freezer at  $-20^{\circ}\text{C}$  and allowed to warm to room temperature. During warming, temperature readings are taken every few seconds. A plot of temperature versus time reveals a graph similar to Figure 8.15a. The temperature rises

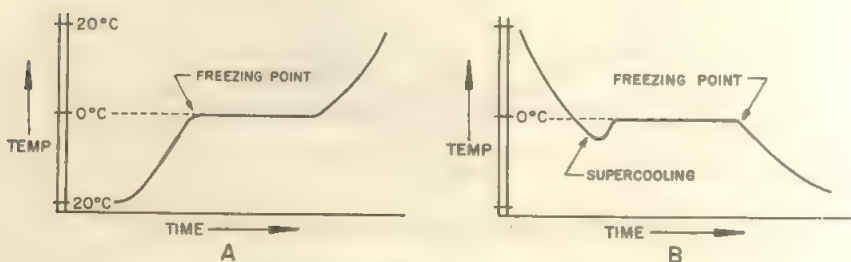


Figure 8.15. Time-temperature freezing (melting) point curves.

steadily to  $0^{\circ}\text{C}$ . At that point liquid first appears. Melting progresses, but no temperature change occurs until no ice remains. When all is melted the temperature of the liquid starts rising and continues rising until it reaches the temperature of the surroundings.

One can observe the same melting (freezing) point by placing a beaker of water with a thermometer (or thermocouple) into a freezing bath and following the temperature. If temperature readings are recorded at time intervals and plotted against time, the result *may be* a curve such as the one represented by the solid and dotted lines (Fig. 8.15b). The temperature falls steadily to  $0^{\circ}\text{C}$ , and ice appears. The temperature reading remains constant until all the liquid is frozen and then drops steadily to the temperature of the bath. Usually, however, the temperature of the water drops steadily until it is somewhat below  $0^{\circ}\text{C}$  (solid line on Fig. 8.15b). Suddenly, at no set temperature, ice appears and the temperature rises to  $0^{\circ}\text{C}$ , remains there until all is frozen and then drops steadily as before. One may note that only at  $0^{\circ}\text{C}$  are both water and ice present. This is the melting point. Should one try to raise the temperature of an ice-water mixture by heating, melting will occur, but the temperature will remain at  $0^{\circ}\text{C}$  until all the solid has disappeared. One who tries to cool a mixture of ice and water is frustrated. The water begins to freeze, but the temperature remains at  $0^{\circ}\text{C}$  until all the liquid has disappeared. The phenomenon noted here, namely of water's cooling below its freezing point, is called supercooling. Liquids in general will supercool. The extent of supercooling may often be modified by rapid

stirring and can be arrested by adding a small crystal of the solid at the freezing point. In both curves the complete freezing or melting is shown to occur at the same constant temperature, the melting point.

On the other hand, plastics soften gradually and eventually pour when heated sufficiently. Tar does likewise. Pyrex glass begins to soften at  $500^{\circ}\text{C}$ ; it is risky to keep it at that temperature for a prolonged time lest the vessel start to deform. However, it is not so soft but that it might be kept for a short time at  $550^{\circ}\text{C}$  without losing its shape. It melts and runs at about  $700^{\circ}\text{C}$ . Plastic, tar and glass are not true solids. Not only do they lack a definite melting point, but they have no definite crystal habit. They are liquids that become thicker and thicker with cooling until they are hard and brittle.

### C. VAPOR PRESSURE

Like liquids, solids have a vapor pressure. The sublimation of dry ice, the disappearance of snow in sub-zero weather, the disappearance and the odor

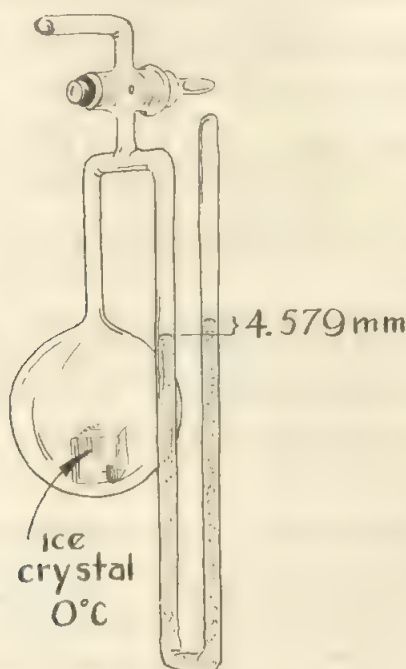


Figure 8.16. Vapor pressure of ice.

of mothballs are evidences of the vaporization of solids. When placed in a vapor pressure apparatus (Fig. 8.16), ice exerts a definite vapor pressure at a given temperature, just as water does. The vapor pressure of ice varies with temperature. At  $0^{\circ}\text{C}$  the vapor pressure is 4.579 mm (the same as for water). Some values are recorded in Table 8.3.

Table 8.3. Vapor Pressure Table of Ice

Temperature	Vapor Pressure mm
0 C	4.579
10 C	1.947
20 C	0.770
30 C	0.280
40 C	0.094
50 C	0.029

## D. HEAT EFFECTS

It was implied in previous sections that heat must be added to raise the temperature of a substance. This is always the case regardless of the state the substance is in. The heat required to raise the temperature of 1 gram of material 1 C is called the specific heat. The specific heat varies somewhat with temperature and varies greatly with changes in state.

The specific heat of water at 15 C is *exactly* 1 calorie. That is, 1 calorie of heat is required to raise 1 gram of water from 14.5°C to 15.5°C. This is the exact definition of the calorie. At other temperatures, water has very nearly the same specific heat. The specific heat of ice at near 0°C is about 0.5 calories. And the specific heat of steam near 100°C chances to be 0.5 calories per gram per degree.

Heat is also exchanged in changing from one state to another. Heat is required to melt or fuse a solid, and heat is required to vaporize either a solid or a liquid. The heat required to melt 1 gram of a solid is called its specific heat of fusion. The specific heat of fusion of water at 0°C is 80 calories. The heat required to vaporize 1 gram of a liquid is called the *specific heat of vaporization*. The heat required to vaporize 1 gram of water at the boiling point is 540 calories.

Consider the magnitude of the heat of vaporization of water, 540 calories per gram. 5.4 grams of water can be heated from 0°C to 100 C with the same number of calories that are required to vaporize only one gram once 100°C is reached, the temperature of the steam being 100°C.

One can see why steam burns are more serious than hot water burns. About nine times more heat is gained from the condensation of the steam at 100°C than is gained in cooling it down from 100°C to body temperature, 37°C.

A refrigerator is kept cool by the continual vaporization of a liquid. Sulfur dioxide, ammonia or freon gas is compressed until liquefied in a motor driven compressor outside the refrigerator compartment. During this process the heat of vaporization is lost. The liquid is then forced into pipes in the refrigerator where the pressure is reduced, allowing it to evaporate. It



takes the heat of vaporization from the surroundings, cooling them. The gas is then drawn outside, compressed and condensed to release the heat gained inside the refrigerator. The process of vaporization inside taking up heat and liquefaction outside giving up heat is repeated over and over in the refrigerator cycle. Operation of the refrigerator warms the room while it cools its own interior.

### EXERCISES

1. State each—Boyle's Law, Charles' Law, Dalton's Law.
2. Describe two kinds of manometers.
3. Explain how a barometer works.
4. An open-end manometer and a closed-end manometer are used to measure the pressure of the same gas sample. Why are the vertical distances between mercury levels different?
5. What happens to a gas when it is heated in a sealed and rigid container?
6. How is a thermometer calibrated in degrees centigrade?
7. Which degrees are larger, °F or °C? How much larger?
8. How are Degrees Absolute absolute?
9. Which of these will fill a 10 liter flask at 25 °C: 20 g hydrogen gas, 10 g hydrogen gas, 0.01 g hydrogen gas, or  $5 \times 10^{-4}$  g hydrogen gas?
10. When a gas sample is collected over water, will its volume be the same as when collected over mercury at the same temperature and pressure? Explain.
11. How can the vapor pressure of a liquid be changed?
12. Explain how the rising of a liquid in a capillary tube shows surface tension.
13. Name five liquids which have a high viscosity.
14. Describe Brownian movement.
15. Define a true solid.
16. What is super-cooled water?
17. Define: (a) specific heat, (b) heat of fusion, (c) specific heat of vaporization.

### PROBLEMS

1. 36 ml of a gas at 25 °C and 1 atm is heated to 85 °C and 1 atm. Calculate its final volume.
2. What is the volume at STP of 64 ml of a gas measured at 27 °C and 760 mm?
3. 72 L of a gas at 760 mm and 0 °C is compressed until the pressure is 1220 mm at 0 °C. Calculate the final volume of the gas.
4. What is the volume of a sample of gas at 380 mm and 300 °A which occupies 26 ml at 640 mm and 300 °A.
5. What volume will a sample of gas occupy at 1220 mm and 23 °C, if it occupies 45 ml at 27 °C and 700 mm?
6. Calculate the volume at STP of 150 ml of gas measured at 645 mm and 28 °C.
7. Calculate the temperature in °C of the following Fahrenheit temperatures: 212 (boiling point of water), 98.6 (body temperature), 32 (freezing point of water), 0 and -40.
8. Find the volume at STP of the pure hydrogen in a 10 L mixture of hydrogen, helium and nitrogen at 27 °C, in which the partial pressure of hydrogen is 150 mm and the total pressure is 630 mm.
9. A tire pump has a cylinder 20 inches in length. How far can the piston be pushed down before air enters the tire, which is at a gauge pressure of 29.4 pounds per square inch? The barometric pressure is 14.7 pounds per square inch.
10. A sealed two quart can is half full of water and has a total pressure of 760 mm at 25 °C. It is heated to 100 °C without bursting. What is the total internal pressure of the can at that temperature?
11. 500 ml of oxygen gas saturated with water vapor at 40 °C and 680 mm is compressed to 250 ml at the same temperature. Calculate the final pressure.
12. 100 ml of oxygen gas is collected over water at 25 °C and at a barometric pressure of 635 mm. (a) What is the pressure of oxygen? (b) What volume would the dry oxygen occupy at the same barometric pressure and temperature?

13. Find the volume at STP of 175 ml of hydrogen measured over water at 28 °C and 648 mm.
14. 100 ml of  $O_2$  at STP is added to 400 ml of  $N_2$  at STP, and the mixture is collected over water at 26 °C and 645 mm. (a) What is the oxygen pressure in the wet gas mixture? (b) What is the volume of the wet gas mixture?
15. The volume of an air-tight irregularly shaped cavity was determined by releasing into it 100 L of neon at 25 °C and 1 atm. After mixing, the partial pressure of neon was 87 mm. Calculate the volume of the cavity.
16. How much heat must be absorbed by 15 g of ice at -15 °C to convert it to steam at 110 °C?
17. How many g of steam at 100 °C need be added to 600 g of water at 20 °C to raise the temperature to 85°?
18. Nitrogen gas is added to 8 liters of oxygen gas at 380 mm and 25°C until the total pressure is 640 mm. What is the final pressure of the oxygen gas?

## THE KINETIC THEORY

The development of the Kinetic Theory of matter from its beginning in the seventeenth century is a fascinating story of a successful application of the scientific method. The theory developed hand in hand with discovery of the phenomena and the formulation of the laws presented in Chapter 8. Newly found facts brought new laws. New laws required re-examination of old theories. Some postulates were rejected, some amended and some verified, until the Kinetic Theory has emerged as one of the basic theories of physics and chemistry. The Kinetic Theory holds an exalted position in scientific theory because of its simplicity and because it explains so well the many facts and laws that are known concerning the behavior of matter in its three states. Some of these facts and laws discussed previously in this text are:

1. Matter in all states possesses a heat capacity.
2. Gases are fluid.
3. Gases fill completely any containers to which they are admitted.
4. Gases are compressible.
5. Gases exert a pressure.
6. When the pressure exerted on a gas sample at constant temperature is increased, the volume of the gas sample is reduced. The volume varies inversely with the pressure, as described by Boyle's law.
7. When the temperature is raised, the volume and/or the pressure of a gas sample is increased. If the pressure remains constant, the volume varies with the temperature, as described by Charles' Law.
8. Each gas of a mixture fills the entire volume of its container and exerts the pressure it would exert if alone in the container. The total pressure

is the sum of the pressures each gas would exert if alone in the container. (Dalton's Law.)

9. Gases follow Boyle's, Charles' and Dalton's Laws with little deviation at temperatures well above the boiling point of the gas and at less than a few atmospheres pressure. Deviations can be very great at low temperatures and high pressures.
10. Liquids are more dense than gases.
11. Liquids are almost incompressible.
12. Liquids exhibit Brownian movement.
13. Liquids are fluid, but exhibit viscosity.
14. Liquids exhibit surface tension.
15. Liquids have a set vapor pressure at constant temperature.
16. The vapor pressure of a liquid increases rapidly with temperature.
17. There is a heat of vaporization.
18. Solids possess a rigid, definite structure.
19. Solids exert a vapor pressure.
20. There is a heat of sublimation.
21. Pure solids melt completely at constant temperature.
22. There is a heat of fusion.
23. Liquids often supercool.

The Kinetic Theory must agree with each of these facts and many others. Failure to agree with any *one* fact proves the theory incorrect, unless it can be amended to agree.

To conserve time and to avoid repetition of details, the development of the Kinetic Theory will not be discussed here. Rather, the postulates of the theory which apply to all three states of matter will be listed first, followed by a list of the postulates that are specific for each phase, gaseous, liquid, and solid. The theory will be examined (when it seems best) to see if it explains adequately the observed facts and laws in the list above.

### POSTULATES OF THE KINETIC THEORY

1. *Matter in all states is composed of particles.* This is the central **postulate** of Dalton's Atomic Theory. These particles may be either molecules, atoms or ions, but the term molecule will be used interchangeably with the term particle in this chapter.
2. *These particles exhibit mutual attraction.* The magnitude of the attraction varies from substance to substance depending upon ion charge, polarity, size and mass and other factors.
3. *These particles have kinetic energy.* The kinetic energy is distributed at random among the particles in the forms of translational and/or vibrational and/or rotational motion. The idea that particle motion exists in all forms of matter is a great contribution to physical theory. The



possible forms of motion (energy) for an oxygen-type molecule are illustrated in Figure 9.1.

4. *The average kinetic energy increases with temperature and changes with a change in state.* According to the theory, matter may remain in either of the condensed states over a range of temperature. Addition of heat energy simply causes an increase in energy in the forms already existent. Eventually, however, the energy increase cannot be accommodated without a change of state. Therefore, a great and sudden change takes place; the solid melts, the liquid vaporizes. The amount of

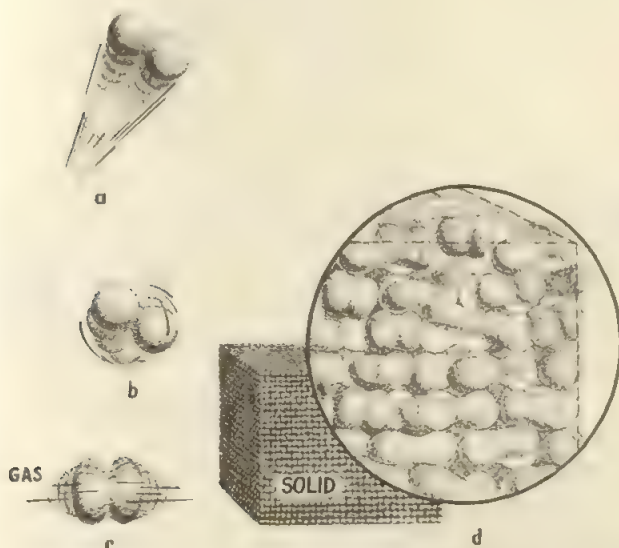


Figure 9.1. Forms of motion exhibited by oxygen molecules: a. translational, b. rotational, c. and d. vibrational.

energy possessed by particles with set mutual attraction determines the state. For a given substance, particle energy increases progressively from solid to liquid to gas.

5. *Collisions between the particles are perfectly elastic.* Energy is transferred from particle to particle by collision, but no energy is lost in the collisions. All the energy is accounted for in the resulting motions of the colliding particles.

The fact that matter in all states possesses a heat capacity, that is, that energy is required to raise the temperature of all matter (Chapter 8), agrees with the above statements. An increase in temperature is accompanied by an increase in kinetic energy. The energy level is raised by added heat. The 1 calorie of heat that raises 1 gram of water from 14.5°C to 15.5°C merely increases the molecular motion of water by that amount of energy.

## MATTER IN THE GASEOUS STATE

Three of the postulates of the kinetic theory as stated for all states must be specified:

1. *The average kinetic energy of the particles is very, very great* (see [3] above).
2. *As a result, the existing mutual attraction is negligible.* Therefore the particles tend to be very far apart in the available empty space (see [2] above).
3. *Not only does the total kinetic energy increase with temperature but the translational portion is proportional to the absolute temperature* (see [4] above).

If these postulates describe the system correctly, it is apparent that: (a) gases fill the container; (b) gases are fluid and (c) gases interdiffuse.

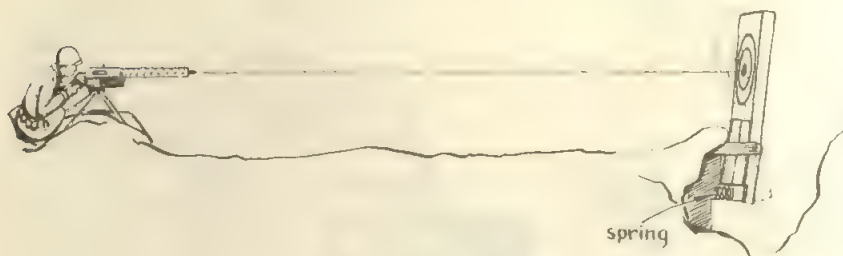


Figure 9.2. Machine gun firing at a target on a spring.

Further, if particles are a relatively great distance apart, gases can be compressed. Compression merely forces the molecules closer together. Expansion allows them to move farther apart, as they will because of their rapid motion.

*Gases exert pressure*, which increases with compression and decreases with expansion. One must think of the pressure being exerted not by the gas as a whole, but by the individual molecules in motion, somewhat like the rifle bullets in the following example. Consider a target mounted on a spring leaning forward, as shown by the dotted outline in Figure 9.2. When a rifle bullet strikes the bull's-eye, the target is pushed back momentarily, then lurches forward when the force of the bullet embedded in it is spent.

Now suppose the target is fired upon with a machine gun so that the firing rate, very slow at first, gradually increases. At first the target lurches backward and forward with each hit. Soon, however, as the firing rate increases, the next bullet hits it before it has completely recovered from the last. The target vibrates wildly, never quite returning to its original position. As the firing speed increases, the vibration lessens until the target is held quite steadily against the compressed spring. Greater firing speed now merely tends to force it back farther. A steady force is being exerted on the target by the colliding bullets. The distance the target is pushed back against the

spring is a measure of the force exerted upon it. The more rapid the firing, the higher the velocity of the bullets, the greater the force.

Pressure is defined as the force per unit area. Each square centimeter of the inner walls of a gas container is a target sustaining a great number of collisions per second with molecule "bullets." The force on this square centimeter area is the pressure. If the container is non-rigid, the walls are pushed out and stretched until the inner force or pressure is equaled by the tension or force outside.

When a gas is compressed, as by a tire pump, more molecules are crowded into a smaller volume. For example, when 2 liters of gas are compressed to 1 liter, twice as many molecules are present in a liter to collide with the walls of the container, and the pressure doubles (Fig. 9.3). The volume varies inversely with the pressure (Boyle's Law).

The translational energy (the moving energy) of molecules is proportional to the absolute temperature. Therefore, at 10°C or 283°A, the energy of molecules is  $283/273$  as great as at 0°C. The molecules hit harder and more often with greater velocity, thus increasing the pressure if the container is rigid. If the pressure is to remain the same, the volume must be increased proportionately to the increase in absolute temperature (Fig. 9.4).

*A gas exerts the same pressure in a mixture of gases that it would if it were in the container alone.* That is, *the pressure of a gas mixture is equal to the sum of the pressures each gas would exert if in the container alone.* As shown in Figure 9.5a, b, c, each gas in a container at constant temperature exerts a pressure depending only on the number of particles present. When the three gases are enclosed together in a container of the same volume (Fig. 9.5d), all three kinds of molecules are present. All kinds collide with all others and with the sides of the container. All contribute as before to the total pressure, in accordance with Dalton's Law. Furthermore, since Boyle's and Charles' Laws, hold for each gas, they hold for the mixture also.

No gas behaves precisely in accordance with Boyle's and Charles' Laws. Only a so-called "perfect" gas does; therefore these laws are called the "perfect gas laws." No real gas is perfect, but most are very nearly so. Only the finest measuring equipment can detect deviations at less than a few atmospheres pressure and a temperature somewhat above the boiling point of a particular gas. These deviations exist because: (1) attractions, although they are small compared to the energy of gas molecules, do exist between the molecules, and (2) although the molecules are small in the space that surrounds them, compression cannot decrease the molecular volume as it can the free space between them.

At low temperatures near the boiling point of the gas the kinetic energy is decreased (the molecules slow down) until attractions between them are no longer negligible. They tend to stick together, decreasing the volume (Fig. 9.6a). At high pressure the molecules are no longer a great distance apart, but may be very close together. A doubling of pressure under these conditions can result in only a slight decrease in volume (Fig. 9.6b).

There are equations that account for these differences from "perfect gas"

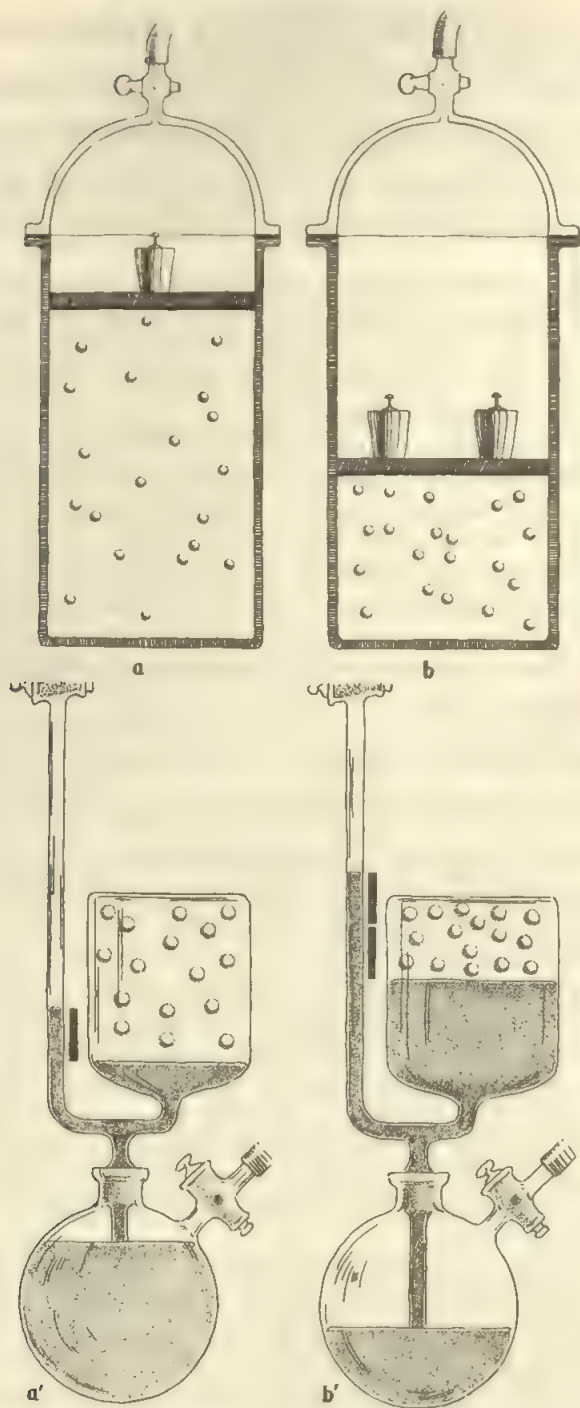


Figure 9.3. Two sets of illustrations showing the effect of increasing pressure on the volume of the gas (Boyle's Law).



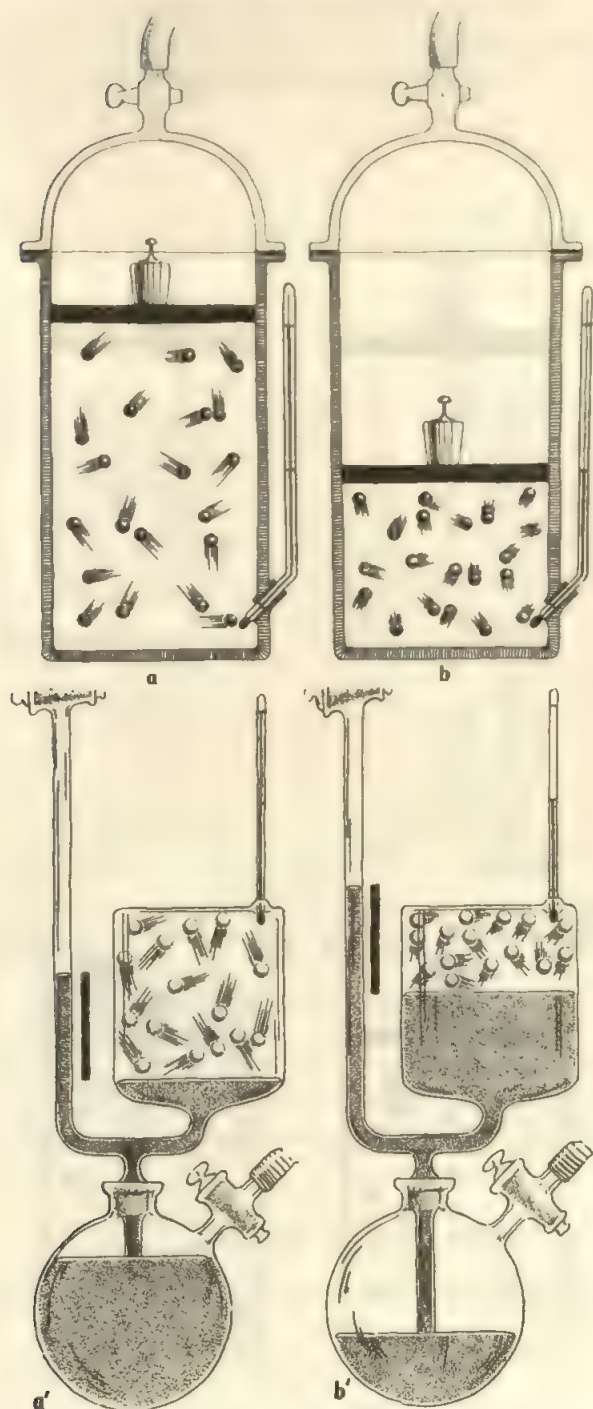


Figure 9.4. Two sets of illustrations showing the effect of a decreasing temperature on the volume of the gas (Charles' Law).

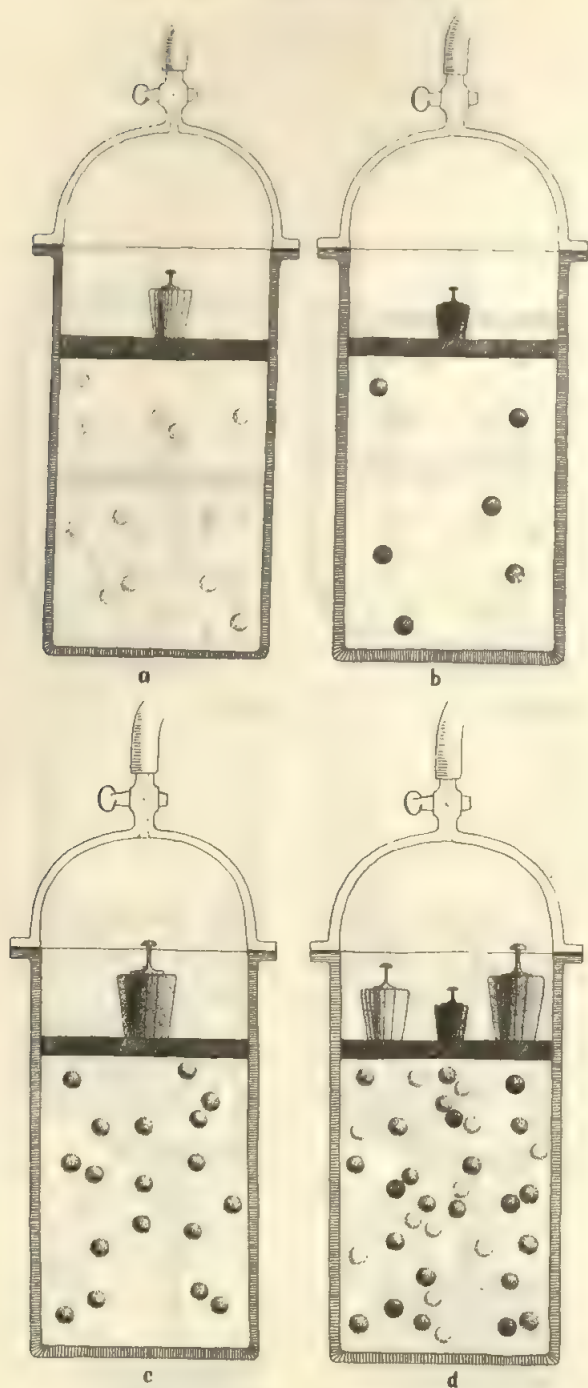
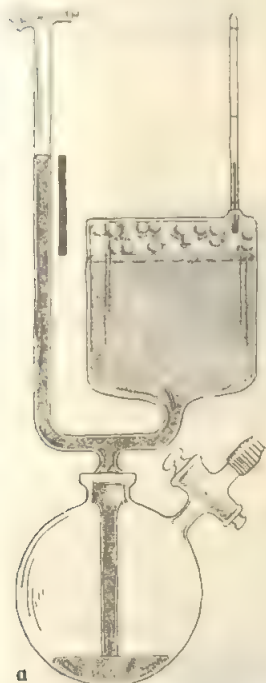


Figure 9.5. Three gas samples of a given volume may occupy the same volume at a pressure equal to the sums of their individual pressures. (Dalton's Law).

behavior, but they are much more complicated than Boyle's and Charles' Laws. Unless one is interested in the behavior of gases at high pressures or low temperatures, the answers obtained by the simple calculations studied here are satisfactory.



At low temperatures a gas occupies a smaller volume than predicted. (Compare with Fig. 9.4b.)



At very high pressures gases occupy a larger volume than predicted. (Compare with Fig. 9.3b.)

Figure 9.6. Deviations from Charles' and Boyle's Laws.

The kinetic theory explains these and many other facts so well that it is accepted as an explanation of the true nature of the gas. However, should a single fact about gases be found irreconcilable with the theory, it would be disproved.

## MATTER IN THE LIQUID STATE

Only two postulates of the kinetic theory as it applies to all states need to be specified.

1. *The average kinetic energy of the particles is much less than in the gas phase (see [3], p. 116).*
2. *The existent mutual attraction of the particles is sufficient to hold them close together (see [2], p. 116).*

The energy is still great, for as the particles bump into their neighbors, roll and tumble over one another, vibrate and spin, they may strike minute but visible clay particles (many, many times bigger than they) with sufficient force that these particles may be seen to follow a wild, zigzag path, i.e., to *exhibit Brownian movement*.

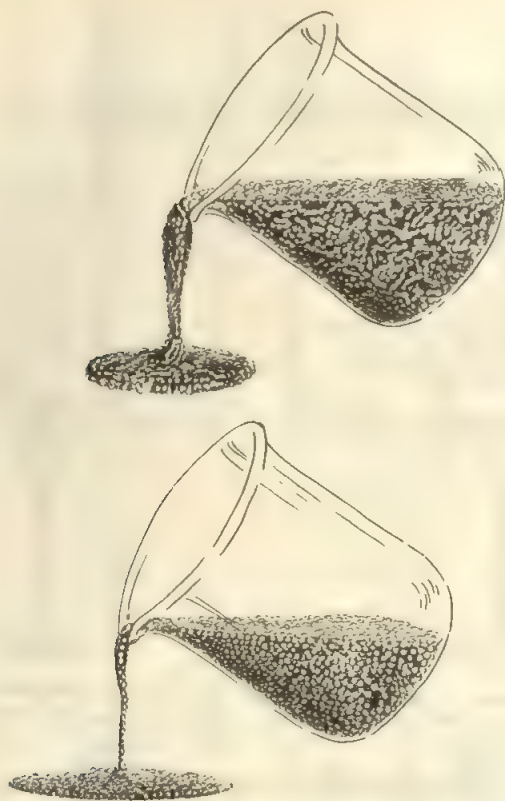


Figure 9.7. Relative viscosity versus molecular structure.

The importance of mutual attraction between particles in liquids is shown by the fact that liquids have a constant volume and assume the overall shape of the lower part of their containers. Mutual attraction is the important factor in *surface tension*. When liquid particles rest upon a surface for which they have little attraction, they tend to pull themselves together into a sphere.

Intermolecular attraction is one of two factors involved in viscosity. Molecules of a liquid must slide past or roll over one another when the liquid is poured. Molecules with strong forces of attraction for one another tend to be more viscous. The configuration or shape of the molecules is another factor influencing viscosity. If the molecules are spheres or are smooth in shape, there is little resistance to flow. If the molecules are irregularly shaped,



long and zigzag, they experience difficulty in sliding past one another (Fig. 9.7). Liquids with such molecules exhibit a high viscosity.

Close examination of the Kinetic Theory shows it to be consistent with the phenomenon of evaporation. Although a molecule in a liquid is moving very rapidly, the average energy it possesses is insufficient to pull it away from its neighbors. However, all molecules do not possess the same energy. In fact, the energy a molecule possesses changes many times per second as it loses or gains energy in repeated collisions. Because the collisions between molecules

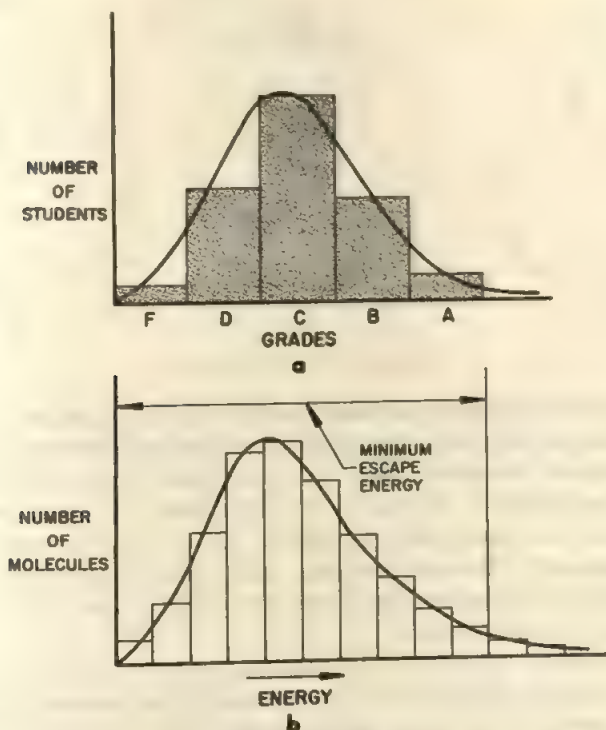


Figure 9.8. Probability curves.

are random, the distribution of energy among them at any one instant is random. If random, the energy distribution follows the so-called "bell-shaped" curve derived by mathematicians and used by teachers of large classes in evaluating student performance and assigning grades. As shown (Fig. 9.8a), there are few students with F's, more with D's, many with an average C grade, fewer again with B grades and few with A grades.

As for the molecules of a liquid (Fig. 9.8b), very few have low energies, many have near average energies, and very few have very high kinetic energy—energy sufficient to overcome the attraction of their neighbors. Most molecules experience their instant of high energy while buried in the liquid, only to lose it to another in a split-second collision.

The very few molecules which gain sufficient energy to escape while at the upper surface of the liquid are responsible for the vapor pressure. Consider water occupying the lower part of an otherwise evacuated flask (Fig. 9.9a). High energy molecules are leaving the surface to occupy the space above. The presence of the vapor molecules creates a pressure above the liquid, a pressure that increases as more molecules enter that space. However, the molecular movement is two directional; molecules collide with each other and the container walls and fall back into the liquid layer (Fig. 9.9b). At

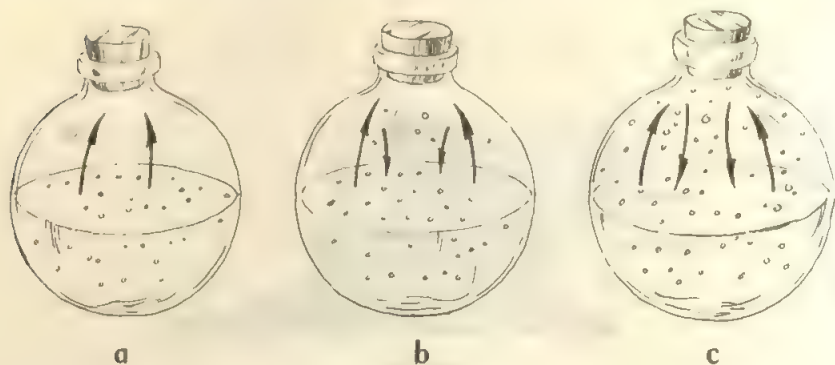


Figure 9.9. Vapor pressure.

first the number returning per second is relatively small, but as the number above the layer increases, the number returning increases. Eventually molecules return as rapidly as they leave the liquid. At this point (Fig. 9.9c) dynamic equilibrium is reached. The total number of molecules per unit volume above the liquid does not change, neither does the pressure. This constant pressure is the vapor pressure. With water, the pressure that exists at 25°C when the number of molecules leaving the water layer equals the number returning is 23.8 mm.

The presence of other kinds of molecules above the liquid does not alter the vapor pressure. The rate at which molecules leave the liquid depends only on the temperature; the rate of return depends on the pressure of the vapor just above the liquid as well as the temperature. A slower rate of diffusion up through a layer of other molecules will lengthen the time required for the vapor pressure to be established throughout the system, but once it is established it will be the same as if no other gas were present.

Remember that the high energy molecules are the only molecules that can escape from the liquid. Energy in gases and liquids is in the form of particle energy. The high energy particles are the "hotter" particles. Continual loss of "hotter" particles will lower the temperature unless heat is allowed to flow into the liquid. The specific heat of vaporization is the amount of heat that must be added to the liquid left behind to keep it at the same temperature during the evaporation of 1 gram of the liquid. It is the energy necessary to maintain average particle energy while losing 1 gram of "hot" particles. The specific heat of vaporization of water is 540 calories at 100°C.

Examination of the vapor pressure table (Chapter 8), part of which is repeated here (Table 9.4 and Fig. 9.10), shows that the vapor pressure of water increases with the temperature. This is true of all liquids and would be predicted by the Kinetic Theory. The higher the temperature, the greater

**Table 9.4. Vapor Pressure of Water**

<i>Temperature</i>		<i>Pressure</i>
°C	°A	mm
0	273	4.6
10	283	9.2
20	293	17.5
30	303	31.8
40	313	55.3
60	333	149.4

the molecular energy, the greater the rate of escape, and the greater the vapor pressure. However, the increase in vapor pressure is more than might be expected.

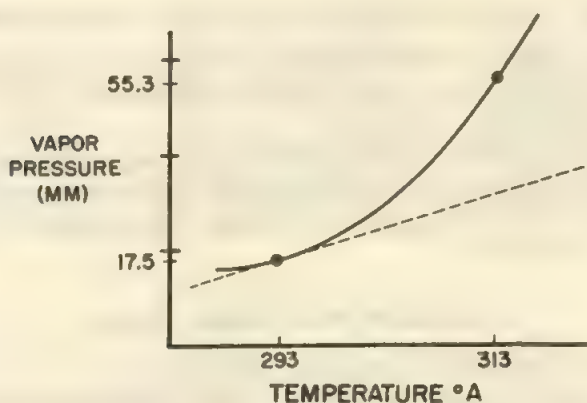


Figure 9.10. Vapor pressure curve for water.

At 40°C (313°A) the vapor pressure is 55.3 mm; at 60°C it is 149.4 mm. For an increase in absolute temperature of:

$$\frac{20}{313} \times 100\% = 6.49\%$$

the change in vapor pressure is:

$$\frac{149.4 - 55.3}{55.3} \times 100\% = 170\%$$

The average molecular energy does not increase 170% with 6.49% increase in absolute temperature. The vapor pressure depends on the number of molecules with an energy sufficient to escape and that number may nearly double with that small change in temperature. The effect of an increase in

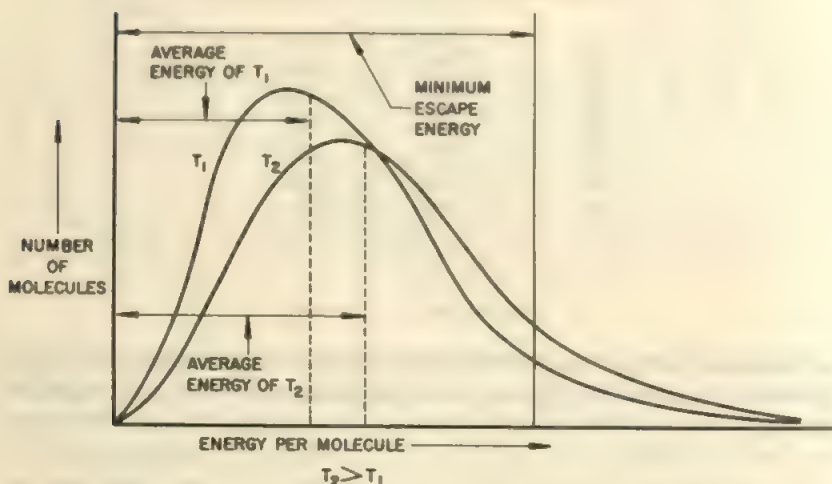


Figure 9.11. Energy distribution between molecules at two temperatures.

temperature on both the average energy of molecules in a liquid, and the magnitude of the fraction of those molecules with sufficient energy to escape is shown qualitatively in Figure 9.11.

In this figure the average molecular energy is seen to increase by only a small fraction, while the number of molecules with an energy greater than that sufficient to escape has more than doubled. Again, the Kinetic Theory is consistent with the facts.

## MATTER IN THE SOLID STATE

Matter in the solid state is composed of particles:

1. that possess less average energy than in the liquid state (see [3], p. 116).
2. whose kinetic energy is so small that the mutual attraction holds the particles close to one another and rigidly in space (see [2], p. 116).

These are the only postulates of the Kinetic Theory as it applies to all matter that must be specified (limited) to apply only to solids.

The only motion available to a particle in this state is vibration about its average position. The particle acts as if it were continually agitated while



suspended on crossed elastic bands, moving back and forth and up and down, but without leaving its position in the lattice.

Because they are pulled tightly together and because there are preferential attractions, such as between plus and minus ions and between plus and minus ends of polar molecules, solid particles tend to "pack" together in the repeating pattern or lattice. The sodium and chloride ions of solid table salt are not grouped at random; equal forces of attraction for each identical ion

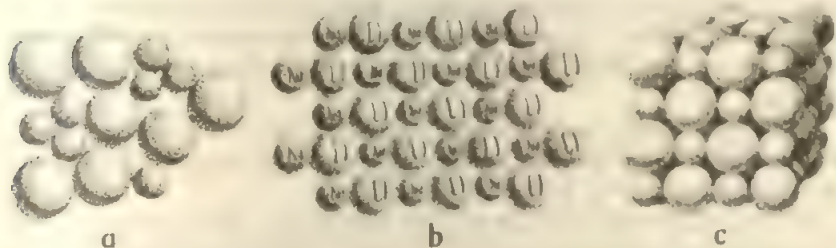


Figure 9.12. Salt crystal.

force them to assume an arrangement where all distances between the centers of opposite ions are equal (Figs. 9.12b, c). This results in a lattice. The same is true for hydrogen chloride. The polar hydrogen chloride molecules are arranged in solid HCl, as shown in Figures 9.13b, c, not as shown in Figure 9.13a. This submicroscopic pattern of particles is continued throughout a large crystal. Molecules or ions are in layers. The crystal breaks between layers; it grows a layer at a time.

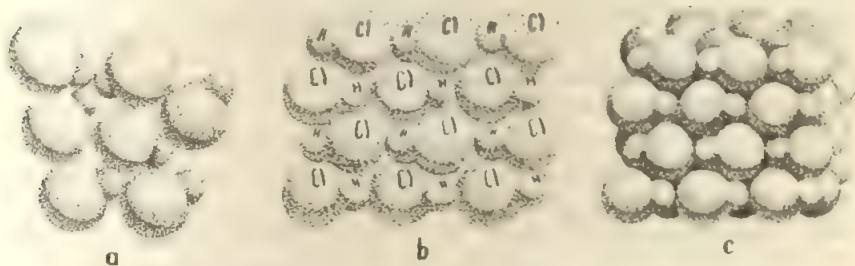


Figure 9.13. Solid HCl crystal.

The existence of vibrational energy admits an explanation of the loss of individual molecules to *form a vapor about the solid and exert vapor pressure*. A molecule in the surface layer of a crystal is attracted to its neighbors in the outer layer and to those behind it. These forces are great. A molecule with an average energy of vibration cannot pull away. However, all molecules do not have the same energy of vibration. Energy is passed around by collision of the molecules with their neighbors as they vibrate. A wave of energy may pass through a crystal by being transferred from one neighbor to the next,

much as the starting jolt passes from car to car throughout the length of a train.

The vibrational energy possessed by the molecules on the surface of a crystal varies in magnitude as does the translational energy of molecules in a liquid. At any one instant, at a given temperature, a certain fraction of the surface molecules possesses sufficient energy to vibrate free of the solid. These molecules escape and form a vapor phase. Some molecules colliding with the crystal are held. Molecules leave and molecules return. The rate of leaving depends only on the temperature. The rate of return depends on the pressure also. When the pressure is such that molecules return at the same rate they escape, equilibrium is attained. This pressure is the vapor pressure.

*Pure liquids freeze completely (until no liquid is left) at constant temperature.* Pure solids melt completely at this same temperature, which is called either the melting point or the freezing temperature.

At  $0^{\circ}\text{C}$ , water and ice are at dynamic equilibrium. Water molecules are leaving the ice and becoming part of the liquid phase and are doing so very rapidly. At the same time, water molecules collide with the ice crystals and are held in the lattice and thus leave the liquid phase. If no heat is added to nor taken from the system, the leaving and returning are equal at the melting point. Although the shape of the ice mass may change, the amount remains constant.

A state of dynamic equilibrium exists in all three equilibrium systems: water and vapor, solid and vapor, and solid and liquid. However, temperature alone decides the rate that molecules leave an area of the surface of either a liquid or a solid. Pressure has negligible effect, because the states are incompressible. At  $0^{\circ}\text{C}$ , that rate at which molecules leave an area of water surface equals the rate at which they leave the crystal layer, and there is equilibrium. Above  $0^{\circ}\text{C}$ , molecules leave the crystal faster than they return and it melts. Below  $0^{\circ}\text{C}$ , molecules leave the liquid phase faster than they return from the crystal and the water freezes.

Suppose one tries to raise the temperature of a mixture of ice and water by heating. The temperature may rise slightly above  $0^{\circ}\text{C}$ . As explained above, the rate at which particles leave the solid is greater than the rate at which they return, and the ice begins melting. In so doing it absorbs calories, the heat of fusion, returning the temperature to  $0^{\circ}\text{C}$  as long as any ice remains. A similar explanation can be given for freezing when both solid and liquid are present. As heat leaves the system, momentarily reducing the temperature, freezing occurs, liberating the heat of fusion to return (or hold) the temperature at  $0^{\circ}\text{C}$  until all the water is frozen.

With ice and vapor (similar to water and vapor) at equilibrium below  $0^{\circ}\text{C}$ , the loss of molecules in the solid equals the return from the vapor. If the temperature is raised  $1^{\circ}\text{C}$ , molecules leave the solid faster as the ice begins to vaporize. As the ice vaporizes, however, the pressure increases, gradually increasing the rate of return until equilibrium is restored. Thus ice and vapor (and also water and vapor) may exist together over a range of temperatures.

But as the temperature is changed, the pressure of the vapor must be allowed to change if the coexistence of the two phases is to continue.

*Supercooling* has been mentioned in the discussion at the beginning of this chapter (p. 112). It was stated that the water must be stirred or agitated when cooled if it is to start freezing at 0°C. Often it supercools several degrees below the freezing point before freezing begins. Apparently this is due to the need for the starting of the lattice. If a crystal of the solid is dropped into a supercooled solution, it freezes immediately. Ions or molecules can then add to the pattern. Scratching or stirring increases the probability of the particles' forming the first unit of the pattern. Once the pattern is there, equilibrium conditions are approached and supercooling is impossible.

### EXERCISES

1. Why is this theory called the Kinetic Theory?
2. Write the postulates of the Kinetic Theory as they apply to (a) matter in all states, (b) matter in the gaseous state, (c) matter in the liquid state, (d) matter in the solid state. **Certain postulates in (a) must be repeated.**
3. Describe the types of particle motion that may take place in: (a) gases, (b) liquids and (c) solids.
4. Which has greatest average particle energy: (a) hydrogen at 0°C and 1 atm; (b) hydrogen at 10°C and 1 atm; (c) hydrogen at 0°C and 2 atm; (d) hydrogen at 10°C and 1 atm?
5. Explain, using the Kinetic Theory:
  - a. How gases flow.
  - b. What happens when a gas is compressed at constant temperature.
  - c. How each gas of a mixture fills a container completely.
  - d. Why liquids are more dense than gases.
  - e. Why liquids are nearly incompressible.
  - f. Where the heat of fusion (the energy) goes when a solid melts.
  - g. Why liquids supercool.
6. Define: (a) perfect gas, (b) dynamic equilibrium, (c) kinetic energy, (d) perfectly elastic collisions, (e) particle (as used in this chapter), (f) theory.
7. Which two postulates of the Kinetic Theory of gases become untrue at low temperatures and high pressures?
8. Which postulate of the Kinetic Theory is false for solids at 0°C?
9. What two factors in theory p' have an important part in determining the viscosity of a liquid?
10. At which of these temperatures may an equilibrium exist: (a) -10°C, (b) 0°C, (c) +10°C, (d) 105°C.
  - a. Between ice and water?
  - b. Between ice and vapor?
  - c. Between water and vapor?
11. Explain why spilled mercury collects in little spheres.
12. Why must pure solids melt completely at one temperature?
13. How do the forces of attraction between water molecules vary from state to state?
14. What causes pressure on the inner walls of a gas container?
15. Why does the vapor pressure of ice increase very rapidly with temperature?
16. How many molecules in any state (relative amount) possess the average energy? How long might the molecules possess it?
17. What causes a clay particle to move as it executes Brownian movement?
18. In what state is diffusion most rapid?
19. Which should be expected to have the highest boiling point: (a) a nonpolar substance, (b) a polar substance, (c) an ionic substance? Explain.
20. Can a gas exist at absolute zero? Explain

# CHAPTER 10

## THE MOLECULAR THEORY

Joseph Lewis Gay-Lussac (1778–1850), one of the pioneers in the study of the gases, took up the work of Jacques Alexandre Charles in 1801. It was Charles who stated (1787) that different gases expand or contract to the same extent with the same changes in temperature. It was Gay-Lussac who found the increase in gas volume to be  $1/273$  at  $0^{\circ}\text{C}$  and  $1/373$  at  $100^{\circ}\text{C}$  for each degree rise in temperature. He stated the temperature-volume law in the form used today. For this reason Charles' Law is also known as Gay-Lussac's Law. Both men contributed to its formulation; both should receive the honor.

### 1. THE LAW OF COMBINING VOLUMES

Continuing his studies of gases, Gay-Lussac turned his attention to determining the per cent of oxygen in air. This he did by exploding known amounts of hydrogen in known amounts of air. In 1805 he discovered that oxygen and hydrogen combine in the volume ratio of 1 to 2. For example, 500 ml of oxygen combine with 1000 ml of hydrogen (when both are at the same temperature and pressure). This interesting fact led him to investigate volume relationships in other gaseous reactions. He also discovered that:

- a. 1 liter of hydrogen chloride combines with 1 liter of ammonia to yield ammonium chloride.
- b. 1 liter of carbon monoxide reacts with  $1/2$  liter of oxygen to give 1 liter of carbon dioxide.
- c. 1 liter of oxygen burns with solid sulfur to yield 1 liter of sulfur dioxide.

From these and other similar observations he formulated a relationship (that, once stated, is obvious) called the *Law of Combining Volumes*: When



*two or more gases are involved in a chemical reaction either as reactants or as products, the volumes of the gases produced or consumed are in the ratios of small integers.*

## 2. AVOGADRO'S HYPOTHESIS

The Law of Combining Volumes appeared at about the same time as Dalton's Atomic Theory. If Dalton's Theory were correct, molecules would combine in the ratios of small whole numbers. It remained for an Italian professor of physics, Amadeo Avogadro (1776–1856), to draw the two ideas together when in 1811 he presented this postulate: *Equal volumes of gases at the same temperature and pressure contain an equal number of molecules.*

Table 10.1 lists the molecular weights and densities of several gases. The great extremes in molecular masses are pointed out by the inclusion of hydrogen (the lightest gas) and uranium hexafluoride (one of the most dense gases).

**Table 10.1. The Molecular Weights and Densities of Some Gases at STP**

<i>Gas</i>	<i>Molecular Weight</i>	<i>Density at STP g/L</i>
H <sub>2</sub>	2.016	0.0894
O <sub>2</sub>	31.998	1.429
CO <sub>2</sub>	44.009	1.964
Cl <sub>2</sub>	70.906	3.17
UF <sub>6</sub>	352.00	15.71

According to Avogadro's Hypothesis, there is the same number of uranium hexafluoride molecules in 1 liter of the gas as there are hydrogen molecules in 1 liter of hydrogen at the same temperature and pressure, even though the uranium hexafluoride molecule is approximately 175 times heavier. At first this may appear unreasonable or even impossible unless one remembers that the molecules in the gases are separated by relatively great distances. This is true even of uranium hexafluoride molecules. Apparently Avogadro sensed that which was postulated years later, that is, that all gases at the same temperature have the same average molecular translational energy. The translational energy depends on both the mass ( $m$ ) and the velocity ( $v$ ) of the molecule ( $T. E. = 1/2 mv^2$ ).

Uranium hexafluoride molecules move much more slowly than hydrogen molecules do and collide with one another and with the sides of the container less often, but they hit much harder. The decrease in frequency of collision is offset exactly by the increased energy of impact, thus each molecule, regardless of size, contributes equally to pressure and volume.

## 3. MOLE VOLUME

In a previous chapter, it was learned that a gram-molecular weight (1 mole) of any compound contains  $6.02 \times 10^{23}$  molecules (or formulas). In the preceding discussion, it was found that equal volumes of gases at the same temperature and pressure contain an equal number of molecules. It follows that there is a *mole volume*, that a mole of gas occupies a set volume at a set temperature and pressure. Using density at STP one can find the mole volume at these conditions.

The volume of 1 mole of oxygen gas is the volume of 32 g.

1.43 g of  $O_2$  occupies 1 liter at STP (Table 10.1)

$$\frac{32 \text{ g/mole}}{1.43 \text{ g/L}} = 22.4 \text{ L/mole at STP}$$

There are 22.4 of the 1.43 g liters in 32 g of oxygen. For hydrogen the mole volume is:

$$2.016 \text{ g/mole} / 0.0894 \text{ g/L at STP} = 22.4 \text{ L/mole at STP}$$

The volume of 1 mole of gas, the gram-molecular weight ( $6.02 \times 10^{23}$  molecules), is 22.4 L at STP.

## 4. CALCULATION OF MOLECULAR WEIGHTS

The existence of the mole volume (a set volume for a mole) affords a method for determining the molecular weight of gases.

**EXAMPLE 1.** The density (weight of 1 liter) of a gas composed of carbon and oxygen is 1.964 g/L at STP. Find the molecular weight of the gas.

**SOLUTION:** One mole of the gas is 22.4 L at STP. One needs to find the weight of 22.4 liters.

$$(1.964) \text{ g/L} \times 22.4 \text{ L/mole} = 44 \text{ g/mole}$$

The gas is carbon dioxide ( $CO_2$ ):

$$12 + (2 \times 16) = 44 \text{ g/mole}$$

**EXAMPLE 2.** 2.51 L of a gas at STP composed of carbon and oxygen weighs 3.12 g. Calculate the molecular weight.

**SOLUTION:**

$$\frac{3.12 \text{ g}}{2.5 \text{ L}} = 1.25 \text{ g/L (mass of 1 liter)}$$

$$\frac{3.12 \text{ g}}{2.5 \text{ L}} \times 22.4 \text{ L/mole} = 28 \text{ g/mole (mass of 22.4 L)}$$

The gas is carbon monoxide (CO):

$$12 + 16 = 28 \text{ g/mole}$$

**EXAMPLE 3.** 2 liters of a gas composed of sulfur and oxygen weighs 4.4 g at 640 mm and 25°C. Calculate the molecular weight.

**SOLUTION:**

a. Find the volume the 4.4 g could occupy at STP. (Boyle's and Charles' Law).

$$2 \text{ L} \times \frac{640 \text{ mm}}{760 \text{ mm}} \times \frac{273^\circ \text{A}}{298^\circ \text{A}} = 1.54 \text{ L at STP}$$

b. Find the mass of 1 liter at STP

$$\frac{4.4 \text{ g}}{1.54 \text{ L}} = 2.92 \text{ g/L}$$

c. Weight of 22.4 L at STP

$$2.92 \text{ g/L} \times 22.4 \text{ L/mole} = 64 \text{ g/mole}$$

Altogether the setup is:

$$\frac{4.4 \text{ g}}{\left(2 \text{ L} \times \frac{640 \text{ mm}}{760 \text{ mm}} \times \frac{273^\circ \text{A}}{298^\circ \text{A}}\right) \text{ L at STP}} \times 22.4 \text{ L/mole} = 64 \text{ g/mole}$$

The gas is  $\text{SO}_2$ :

$$32 + (2 \times 16) = 64 \text{ g/mole}$$

**EXAMPLE 4.** The density of  $\text{SO}_3$  is 3.47 g/L at 820 mm and 30°C. Calculate the molecular weight.

**SOLUTION:** First calculate the volume this 1 liter would occupy at STP and proceed as in Example 3.

$$\frac{3.47 \text{ g}}{\left(1 \text{ L} \times \frac{820 \text{ mm}}{760 \text{ mm}} \times \frac{273^\circ \text{A}}{303^\circ \text{A}}\right) \text{ L at STP}} \times 22.4 \text{ L/mole} = 80 \text{ g/mole}$$

The gas is  $\text{SO}_3$ :

$$32 + (3 \times 16) = 80 \text{ g/mole}$$

**EXAMPLE 5.** 6.405 g of  $\text{KClO}_3$  and a trace of  $\text{MnO}_2$  catalyst were heated until 350 ml of oxygen collected over water at 640 mm and 24°C was evolved. After cooling 6.031 g of a  $\text{KClO}_3 - \text{KCl}$  mixture remained. Calculate the molecular weight of oxygen. Vapor pressure of water at 24°C is 22.1 mm.

**SOLUTION:**

a.

$$0.350 \text{ L} \times \frac{273^\circ \text{A}}{297^\circ \text{A}} \times \frac{(640 - 22.1) \text{ mm}}{760 \text{ mm}} = 0.262 \text{ L at STP}$$

b. This 0.262 L at STP weighs:

$$6.405 - 6.031 = 0.374 \text{ g}$$

c. One liter at STP weighs:

$$\frac{0.374 \text{ g}}{0.262 \text{ L}} = 1.43 \text{ g}$$

d. 22.4 L at STP (1 mole) weighs:

$$1.43 \text{ g/L} \times 22.4 \text{ L/mole} = 32 \text{ g/mole}$$

Altogether, the setup is:

$$\frac{0.374 \text{ g}}{\left(0.350 \text{ L} \times \frac{273^\circ\text{A}}{297^\circ\text{A}} \times \frac{(640 - 22) \text{ mm}}{760 \text{ mm}}\right) \text{ at STP}} \times 22.4 \text{ L/mole} = 32 \text{ g/mole}$$

One can calculate the molecular weight of volatile liquids by the same method. Although the liquid cannot be vaporized at 1 atm and  $0^\circ\text{C}$ , the volume it *would have* at STP may be calculated from the volume occupied by the vapor at a temperature above the boiling point.

EXAMPLE 6. 2.5 L of chloroform vapor at  $150^\circ\text{C}$  and 610 mm weighs 6.92 g.

Calculate the molecular weight of the liquid.

SOLUTION: Calculated just like a permanent gas.

$$\frac{6.92 \text{ g}}{\left(2.51 \text{ L} \times \frac{273^\circ\text{A}}{423^\circ\text{A}} \times \frac{610 \text{ mm}}{760 \text{ mm}}\right) \text{ L at STP}} \times 22.4 \text{ L/mole} = 119.5 \text{ g/mole}$$

The liquid is chloroform ( $\text{CHCl}_3$ ):

$$12 + 1.0 + (3 \times 35.5) = 119.5 \text{ g/mole}$$

EXAMPLE 7. A simple laboratory experiment for determining the molecular weight of liquids with boiling points lower than that of water is described below. Three or four ml of the liquid is added to a previously weighed dry Erlenmeyer flask capped with aluminum foil crimped about the mouth. The Erlenmeyer is placed in water and the water heated to boiling for about five minutes (Fig. 10.1). The liquid vaporizes and escapes through the pinhole, taking the air out with it. In a short time the flask is filled only with the vapor (of the liquid) at the boiling point of water. The flask is then cooled, which condenses the vapor and draws air back into the flask. The flask is weighed again when cool. The increase in weight is due to the few drops of condensed liquid that filled the flask as vapor when hot.

Suppose the complete volume of the Erlenmeyer flask (level-full) is 139 ml. During the experiment the barometric pressure was 760 mm. The increase in weight (weight of flask + aluminum foil + condensed liquid) minus (weight of flask + aluminum cap) = 0.680 g. Calculate the molecular weight of the liquid.

SOLUTION: 139 ml of vapor at  $100^\circ\text{C}$  (boiling point) at 760 mm weighs 0.680 g.

$$\frac{0.680 \text{ g}}{\left(0.139 \text{ L} \times \frac{273^\circ\text{A}}{373^\circ\text{A}}\right) \text{ L at STP}} \times 22.4 \text{ L/mole} = 150 \text{ g/mole}$$



The liquid is carbon tetrachloride ( $\text{CCl}_4$ ). It has a molecular weight of  $12 + (4 \times 35.5) = 154$  g/mole. The error occurs because carbon tetrachloride has an appreciable vapor pressure at room temperature. When the flask + foil + condensed liquid were weighed, less air was present in the flask (being

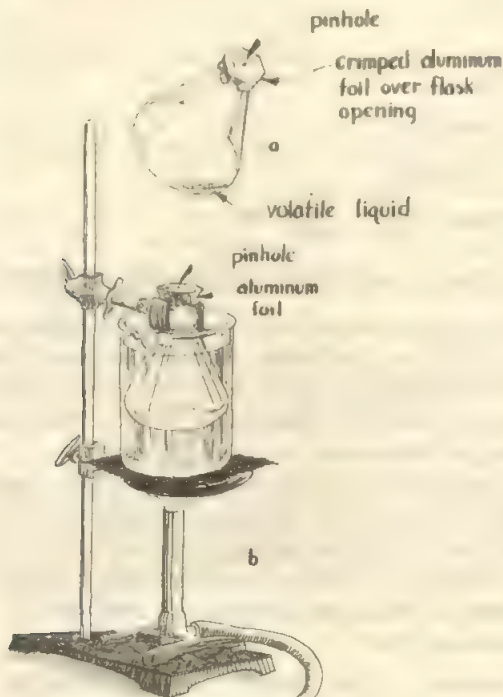


Figure 10.1. Apparatus for determining the vapor density of volatile liquids.

at 760 mm minus the vapor pressure of  $\text{CCl}_4$ ) than was present at the first weighing when the air pressure was 760 mm.

## 5. CALCULATION OF GAS DENSITIES

When either the molecular weight or the molecular formula (from which the molecular weight can be calculated) is known, one can calculate (using the mole volume at STP) the density of a gas at any set conditions of temperature and pressure.

**EXAMPLE 1.** What is the density in g/L of oxygen gas at STP?

A mole of oxygen gas,  $\text{O}_2$ , weighs 32 g; it occupies 22.4 L at STP. 32 g is divided between the 22.4 L.

$$\frac{32 \text{ g/mole}}{22.4 \text{ L/mole}} = 1.429 \text{ g/L}$$

**EXAMPLE 2.** What is the density in g/L of carbon dioxide at 25°C and 640 mm?

1 mole of  $\text{CO}_2$  is  $12 + (2 \times 16) = 44$  g. It occupies

$$22.4 \text{ L/mole} \times \frac{298}{273} \times \frac{760}{640} = 29.0 \text{ L}$$

One liter weighs

$$\frac{44 \text{ g/mole}}{29.0 \text{ L/mole}} = 1.52 \text{ g/L}$$

The complete setup is:

$$\frac{44 \text{ g/mole}}{\left(22.4 \text{ L/mole} \times \frac{298}{273} \times \frac{760}{640}\right)} = 1.52 \text{ g/L}$$

## 6. THE CANNIZZARO PRINCIPLE AND ATOMIC WEIGHTS

The value of Avogadro's Hypothesis was not fully appreciated for over 40 years. It was in 1858 that the Italian chemist Stanislao Cannizzaro (1826–1910) showed how it might be used to determine atomic weights. Until that time the formula of water was thought to be HO. The atomic weight of oxygen was taken as 8 compared to 1 for hydrogen.

By a simple application of Avogadro's Hypothesis, Cannizzaro showed that many elemental gases are diatomic (contain two atom molecules). Consider the reaction of the gases hydrogen and chlorine. It is shown experimentally that 1 volume of hydrogen combines with 1 volume of chlorine to produce 2 volumes of hydrogen chloride, all measured at the same temperature and pressure. That is:

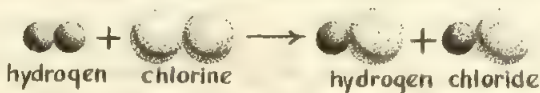
1 liter hydrogen + 1 liter chlorine  $\longrightarrow$  2 liters hydrogen chloride

According to Avogadro's Hypothesis:

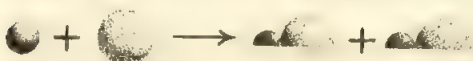
X molecules of hydrogen + X molecules of chlorine  $\xrightarrow{\text{become}}$  2X molecules of hydrogen chloride

The product, hydrogen chloride, is a pure substance; it is composed of identical molecules. Each molecule must contain at least 1 hydrogen atom and at least 1 chlorine atom. But there are twice as many hydrogen chloride molecules formed as there were either chlorine or hydrogen molecules. Each hydrogen molecule and each chlorine molecule must contain at least 2 atoms.

the reaction is this



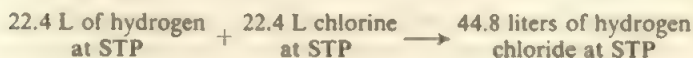
and not this



If the explanation is repeated in mole quantities, it is found that 22.4 L of hydrogen at STP is mixed with 22.4 L of chlorine at STP. The mixture is exploded with an electric spark in a *very rigid* container. On cooling to  $0^{\circ}\text{C}$  and adjusting the pressure to 760 mm, there are 44.8 liters of hydrogen chloride.

In equation form:

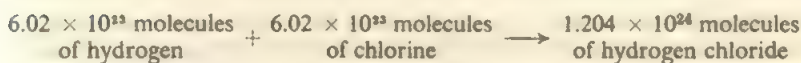
a.



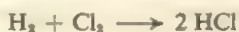
b.



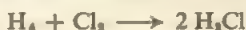
c.



The molecular equation is:



The experiment above does not rule out the possibility the hydrogen molecules could be  $\text{H}_4$ . The equation might then be:



However, because one mole of hydrogen gas has never been observed to be found in more than 2 moles of the product, its formula is taken as  $\text{H}_2$ . One mole of hydrogen gas ( $\text{H}_2$ ), 22.4 liters at STP, weighs 2.016 g. The weight of one mole of H atoms is:

$$\frac{2.016 \text{ g/mole H}_2}{2 \frac{\text{gram-atomic weight}}{\text{mole H}_2}} = 1.008 \text{ g}$$

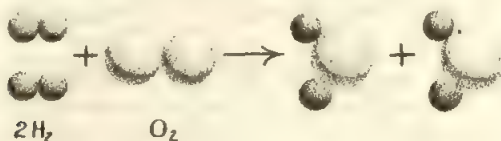
The atomic weight is 1.008. By similar arguments the 22.4 L of chlorine at STP (70.906 g) contains 2 moles of chlorine atoms and the atomic weight is:

$$\frac{70.914}{2} = 35.457$$

In the formation of water from its elements: 2 moles hydrogen + 1 mole oxygen becomes 2 moles of water. The equation must be:



or:



Hydrogen was previously shown to be diatomic ( $\text{H}_2$ ). Here oxygen must be diatomic, because after reaction oxygen atoms appear in twice as many

particles as they did in elemental form. Were the formula of water  $\text{HO}$ , as once it was thought to be, equal volumes of the diatomic molecules of hydrogen and oxygen must react. This is not the case. The formula of water is  $\text{H}_2\text{O}$ ; hydrogen has an atomic weight of 1.008, and the atomic weight of oxygen is  $18.016 - 2.016 = 16.00$ .

It should be noted that the experimental evidence does not preclude tetratomic oxygen ( $\text{O}_4$ ). That is, a mole of oxygen, 32 grams and 22.4 liters, might contain  $6.02 \times 10^{23}$  molecules of  $\text{O}_4$ . If such were the case, water would be  $\text{H}_2\text{O}_2$  and the atomic weight of oxygen would be 8. This is improbable. In no reaction has a molecule of oxygen divided four ways. If it were to do so, the formula  $\text{H}_2\text{O}_2$  must be accepted. Observations indicate that one mole of oxygen is 2 gram-atomic weights, and the atomic weight of oxygen is 16.00.

Using the same reasoning, the analysis of a series of compounds containing a common element may be used to determine the atomic weight.

**EXAMPLE 1.** Below are a series of gases that have been analyzed for an element X. The analyses are given in grams of X per mole.

Gases	Mol. Weight	Gram X/mole	
A	36.5	35.5	35.5
B	71.0	71.0	$2 \times 35.5$
C	50.8	35.5	35.5
D	85.0	71.0	$2 \times 35.5$
E	119.5	106.5	$3 \times 35.5$

Find the atomic weight (maximum atomic weight of element X).

**SOLUTION:** The smallest weight of element X per mole of gas is 35.5, and all weights are multiples of 35.5. This is the atomic weight. The element X is chlorine. The gases are  $\text{HCl}$ ,  $\text{Cl}_2$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$ .

**EXAMPLE 2.** Find the atomic weight of element Y from the following data.

Gas	Mol. Weight	% Y
A	64	50.0
B	44	72.7
C	80	60.0

**SOLUTION:** There are

$$0.50 \times 64 = 32 \text{ g of Y/mole of A}$$

$$0.727 \times 44 = 32 \text{ g of Y/mole of B}$$

$$0.60 \times 80 = 48 \text{ g of Y/mole of C}$$



A mole of a compound must contain at least 1 atomic weight of each element in grams or a multiple of the atomic weight. The largest number that will divide into both 32 and 48 to give a whole number is 16.

The element is oxygen. The gases are  $\text{SO}_2$ ,  $\text{CO}_2$  and  $\text{SO}_3$ .

## 6. AVOGADRO'S NUMBER

The number  $6.02 \times 10^{23}$ , the number of atoms per gram-atomic weight, the number of molecules per mole, is called Avogadro's number. Avogadro never knew this number nor did Cannizzaro, but they realized that a mole must be a certain number of molecules. They postulated the existence of such a number and knew that it must be a large number. The magnitude of the number was determined this century by electrochemical methods and by X-ray study of crystals.

### EXERCISES

1. State the Law of Combining Volumes. Illustrate the law with three examples.
2. State Avogadro's Hypothesis.
3. What is the volume of 1 mole of any gas at STP?
4. A mole of  $\text{CH}_4$  gas at STP is (a) \_\_\_\_\_ g, (b) \_\_\_\_\_ L, (c) \_\_\_\_\_ molecules.
5. Describe the Cannizzaro Method for determining atomic weights.
6. Explain why 1 liter of nitrogen gas and 3 liters of hydrogen combine to give 2 liters of ammonia.

### PROBLEMS

1. What fraction of a mole is:
  - a. 2 liters of gas at STP?
  - b. 3 liters of oxygen measured at  $-23^\circ\text{C}$  and 890 mm?
  - c. 4 liters of nitrogen collected over water at  $27^\circ\text{C}$  and 685 mm?
  - d. What fraction of a mole of water vapor is there in part c?
2. How many grams is:
  - a. 11.2 liters of oxygen at STP?
  - b. 0.95 L of sulfur dioxide,  $\text{SO}_2$ , at STP?
  - c. 2.5 L of ethane,  $\text{C}_2\text{H}_6$ , at  $127^\circ\text{C}$  and 640 mm?
  - d. 45 L of ammonia gas,  $\text{NH}_3$ , at 200 A and 800 mm?
3. How many molecules are there in each gas sample described in a to d in Problem 2 above?
4. Calculate the density of:
  - a. Chlorine gas at STP.
  - b. Water vapor at its boiling point and 1 atm.
  - c. Benzene,  $\text{C}_6\text{H}_6$ , at its boiling point,  $80^\circ\text{C}$ , at 1 atm.
  - d. Of bromine vapor at  $80^\circ\text{C}$  and 480 mm.
5. A hydrocarbon gas is 85.7% carbon and 14.3% hydrogen. It has a density of 1.875 g/L at STP. Find the molecular weight and the molecular formula.
6. A gas has a density of 1.429 g/L at  $819^\circ\text{C}$  and 1520 mm. Calculate the molecular weight of the gas.
7. Calculate the volume of 5.6 g of oxygen gas collected over water at  $27^\circ\text{C}$  and 640 mm.
8. Calculate the density in g/L at STP of the following gases: (a)  $\text{CO}_2$ , (b)  $\text{SiF}_4$ , (c)  $\text{SO}_3$ , (d)  $\text{NH}_3$ , (e)  $\text{UF}_6$ , (f)  $\text{C}_2\text{H}_2$ .
9. Calculate the molecular weight of each of the following gases:
  - a. Gas A has an STP density of 1.429 g/L.
  - b. Gas B has a density of 2.86 g/L at STP.
  - c. 2 g of gas C occupies 1.02 L at STP.
  - d. 2 L of gas D at STP weighs 31.4 g.
  - e. 3 L of gas E at 640 mm and  $27^\circ\text{C}$  weighs 8.19 g.
  - f. 2.5 g of gas F occupies 0.915 L at 640 mm and  $27^\circ\text{C}$ .

10. Choose from this list of gases the formula of the gas described in each part:  $\text{CH}_4$ ,  $\text{NH}_3$ , Ne, CO, NO,  $\text{O}_2$ , Ar.
  - a. density of 1.25 g/L at STP.
  - b. density of 0.714 g/L at STP.
  - c. density of 4.88 g/L at  $-123^\circ\text{C}$  and 1520 mm.
  - d. 3.5 L at 870 mm and  $368^\circ\text{A}$  weighs 4.25 g.
11. Find the volume at STP of 175 ml of hydrogen measured over water at  $28^\circ\text{C}$  and 648 mm.
  - a. How many g of hydrogen is this?
12. 7.6 g of  $\text{O}_2$  and 34 g of  $\text{N}_2$  are mixed and collected over water at  $26^\circ\text{C}$  and 645 mm.
  - (a) What is the pressure of oxygen in the wet gas mixture? (b) What is the volume of the wet gas mixture?
13. Analysis of samples of three pure gases revealed the following weight of element X per liter at STP: (a) 1.071 g, (b) 2.142 g, (c) 1.607 g. Calculate the probable atomic weight of element X.
14. 0.500 L of a gas sample at 640 mm and  $27^\circ\text{C}$  was found to contain 0.631 g of element X, (Problem 13). Is the gas sample pure? Have calculations for evidence.
15. 3 L of hydrogen gas and 1 liter of nitrogen gas, both measured at  $27^\circ\text{C}$  and 640 mm, are passed as a mixture over an impure iron catalyst at high pressure and high temperature. The final gas mixture exerts a pressure of 400 mm at  $27^\circ\text{C}$  in a 4 liter container. What fraction of the hydrogen gas originally in the container has combined with nitrogen to form ammonia gas,  $\text{NH}_3$ ?

## OXYGEN

Thus far in the course, basic ideas of physics and chemistry relative to the properties and behavior of matter have been discussed. The three physical states have been studied with reference to the similarities and differences between their inner structures. The structure of atoms has been considered; the importance of the electron configuration of the atoms of an element in determining the properties was stressed. The Periodic Table has been presented and shown to be an arrangement of the elements in groups of similar electron structure and similar chemical properties.

These basic ideas will be used freely in the descriptive chapters to follow. The properties of an element and its compounds will be reconciled with or predicted from the position of the element in the table.

## 1. CHARACTERISTICS OF OXYGEN

Oxygen is element number 8. It holds 8 electrons per atom. It appears in the upper right-hand corner of the Periodic Table since it is the first element of Group 6 (Table 11.1). The number of electrons in the two levels of an oxygen atom, beginning with the innermost level, are 2 and 6. The inner shell is filled, leaving 6, or two less than a stable octet in the outermost (or valence) level.

## A. PHYSICAL PROPERTIES

The oxygen molecule ( $O_2$ ) is readily formed by the sharing of four electrons, two from each atom. The oxygen molecule is light; furthermore, the 12 valence electrons are held closely to the two nuclei, minimizing attractions for other molecules. For these reasons, little energy is necessary to cause the molecules to move rather freely about each other (to melt the solid), and little energy is required to separate the molecules (to vaporize liquid oxygen).

$$\frac{32 \text{ g/mole}}{22.4 \text{ L/mole}} = 1.429 \text{ g/L}$$

It condenses to a pale blue liquid at  $-182.97^{\circ}\text{C}$  and 1 atmosphere pressure and freezes at  $-218.77^{\circ}\text{C}$ .

### Table 11.1. Oxygen and the Periodic Table

[illegible]

Its position in the Periodic Table indicates that oxygen is a gas. In Table 11.2 all elemental gases (at room temperature) are underlined. Except for hydrogen, whose appropriate position is open to question, all elemental gases appear in the upper right hand corner and in group 0.

**Table 11.2. Positions of Elemental Gases (underlined) in the Periodic Table**

H																	<u>H</u>	<u>He</u>	
Li	Be													B	C	<u>N</u>	<u>O</u>	<u>F</u>	<u>Ne</u>
Na	Bg													Al	Si	P	S	<u>Cl</u>	<u>Ar</u>
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	<u>Kr</u>		
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	<u>Xe</u>		
Cs	Ba	La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	<u>Rn</u>		
Fr	Ra	Ac Lw																	



All are diatomic, except the inert gases, and all hold their electrons closely about them.

Oxygen, being a non-polar gas, is only sparingly soluble in water. At 18°C and 1 atmosphere, 32.2 ml (43.2 milligrams) may dissolve in one liter of water. Nevertheless, this small quantity of dissolved oxygen is essential for marine life. Fish will die in newly boiled and cooled water.

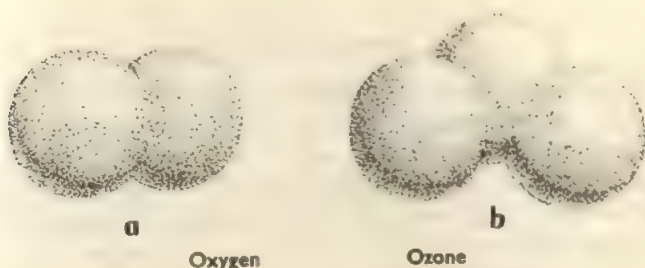


Figure 11.1 Two elemental oxygen molecules.

Although oxygen gas is generally diatomic, *triatomic oxygen* ( $O_3$ ), called *ozone*, may occur under special conditions. Ozone has properties very different from those of oxygen. Its density is 2.144 g/L, 50 per cent greater than the density of oxygen. It boils at  $-112.4^\circ\text{C}$  at 1 atmosphere pressure and freezes at  $-244.7^\circ\text{C}$ . The triatomic molecules are less stable than the more common two-atom molecules, and the gas is more reactive and is a very strong oxidizing agent.

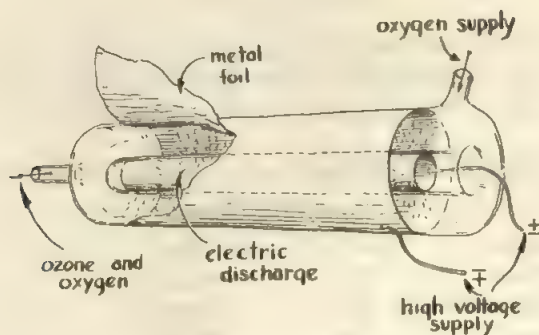
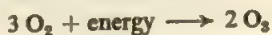


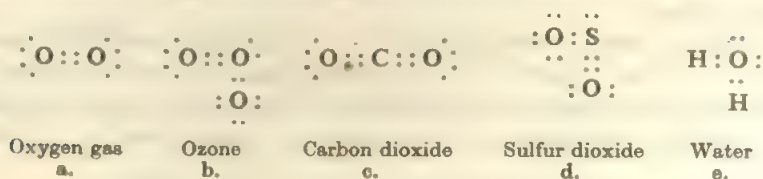
Figure 11.2. Preparation of ozone.

Consistent with its high reactivity is the fact that energy is required to make ozone from oxygen.



The energy may be gained either by absorption of ultraviolet light, or by passing the gas over a hot platinum wire or by passing oxygen through an electric discharge (Figure 11.2). Simple valence electron structures for ozone

and for some other oxygen-containing molecules are shown below:



## B. CHEMICAL PROPERTIES

One can predict the chemical properties of oxygen from its position in the Periodic Table. It is in Group 6, that is, it has 6 valence electrons. It must gain electrons in ionic bond formation (it is a non-metal). Each atom must gain 2 electrons to gain an octet configuration. The ionic valence of oxygen is  $-2$ . Electronegativity increases up and to the right, and oxygen is second only to fluorine in its attraction for electrons in the valence shell. It is an active non-metal. Oxygen is not limited to ionic bonding alone; having 6 electrons, it need share only 2 more to gain the inert gas configuration. Oxygen atoms may share electrons among themselves, or they may share electrons with other atoms (a, b, c, d and e, above) to form compounds. The discussions under the headings Occurrence, Preparations, Reactions and Compounds will illustrate additional chemical properties of the element.

## 2. OXYGEN IN NATURE

### A. OCCURRENCE

Oxygen is the most abundant element. The earth's crust (which includes a 10-mile shell and the atmosphere above it) is estimated to be 49.13 per cent oxygen by weight. Other abundant elements are shown in Table 11.3.

**Table 11.3. Weight Percentages of the Most Common Elements**

Oxygen	49.13	Sodium	2.83
Silicon	27.72	Potassium	2.59
Aluminum	8.13	Magnesium	2.09
Iron	5.0	Titanium	0.44
Calcium	3.63	Hydrogen	0.15

As shown previously, 20.99 per cent of the dry atmosphere is oxygen; the rest is mostly nitrogen. Oxygen constitutes 85.79 per cent of sea water, 47.3 per cent of dry soil, 42.9 per cent of vegetation, 46.6 per cent of igneous rocks and 65.0 per cent of the human body.

Almost all the oxygen in dry air is in the elemental form. A small amount is found in carbon dioxide and other oxide gases. The atmosphere contains a

variable amount of oxygen found in water vapor; the amount depends on the prevailing humidity. In rocks and soil it occurs in complex silicates and aluminates and many other minerals. The water, fats, carbohydrates, and proteins of animal and vegetable life contain oxygen.

### B. LIFE PROCESSES

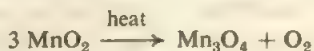
The presence of oxygen in water and in the three classes of foods (proteins, carbohydrates and fats), illustrates the importance of its compounds in life processes. Elemental oxygen is necessary for animal life. Oxygen is brought to the lungs by respiration. Here it is absorbed by the blood, especially by the hemoglobin, and carried to the cells, where foods are converted to carbon dioxide, water and other waste products, thereby producing energy and body heat. Rapid physical exertion requires more energy, and thus more oxygen is consumed to free that energy.

## 3. THE HISTORY OF OXYGEN

Although oxygen is the most abundant of all the elements and although it surrounds us and is a major component of most materials in our environment, it was not the first element discovered. In fact, many rarer elements, such as gold, silver, lead, tin and mercury, were known and prized by the ancients. Carbon (charcoal) and sulfur were used in gunpowder in the sixteenth century. The ancients all used oxygen, but oxygen was not isolated nor was combustion understood until the latter part of the eighteenth century.

Prior to 1777, the mechanism of combustion or burning was explained by the so-called *phlogiston theory*. According to this theory, combustible materials contain phlogiston which they lose to the air while burning. Materials may contain varying amounts of phlogiston. The greater the phlogiston content, the more completely the substance can burn. However, air can contain only a limited amount of phlogiston. When the air becomes saturated with phlogiston and can accept no more, the reaction ceases. The reasoning is clear. The ash has lost something, and combustible substances may not burn completely in a limited supply of air. The phlogiston theory remained secure, and oxygen remained unknown until investigators noted changes in air with oxidation and analyzed them quantitatively.

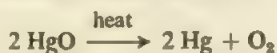
Two men are credited with the discovery of oxygen; a Swedish chemist, Karl Wilhelm Scheele, and an Englishman, Joseph Priestley. Scheele prepared oxygen in 1772 by heating "magnesia nigra" ( $\text{MnO}_2$ ).



In 1774, when Priestley first prepared oxygen, Scheele had already prepared it in at least three different ways. Due to ill health and poverty his results were not well known until after 1777, when he published his only book.

Priestley published his work immediately and soon gained wide acclaim for his discovery.

Priestley was one of the first to see the advantage of collecting gases over mercury instead of over water. Substances over mercury can be heated well over 100°C, and very few gases are soluble in mercury. In 1774, he was carrying out experiments with various "kinds of air." He heated all the substances he could find over mercury. If a gas was obtained, he tested it by admitting a burning candle and by placing mice in the atmosphere. In one of these experiments oxygen was evolved. The details of this experiment are interesting. As usual he inverted a bottle full of mercury in a dish of mercury in such a way that no air entered the inverted bottle. He then pushed mercuric oxide under the edge of the bottle and let it rise to the top of the mercury. He heated the oxide by focusing the sun's rays on it with a large magnifying glass. Soon the mercury level began descending as oxygen formed over it in the bottle. The equation of the reaction is this:



Priestley discovered that a candle burned in the "air" with a remarkably vigorous flame. After he had found it to be "superior" for mice, he breathed the gas himself and fancied that his "breath felt light and easy for some time afterward."

Neither Priestley nor Scheele realized that he had discovered a new element. They both considered the gas to be very pure air. It remained for the great French scientist, Antoine Laurent Lavoisier, to demonstrate that oxygen was a pure substance, a component of air and a reactant consumed when substances were burned. Lavoisier's conclusions were based on a number of experiments. In one of these he placed a piece of tin metal in a flask of air and sealed it. He heated the flask, and weighed the apparatus when cool and found there was no change in weight. On breaking the flask, air rushed in, showing that the air in the flask had diminished. Furthermore, the "tin" weighed more, the weight equalling the loss in weight of the air. Clearly a part of the air was transferred to the tin. He found that only a certain portion of the air would react with heated tin.

Later the same year, 1777, he heated mercury mildly in air and noted the decrease in the volume of air as mercuric oxide formed. He next heated the oxide to a *higher* temperature, decomposing it as Priestley had done in preparing oxygen. He recovered the same volume of gas in the decomposition of the oxide as had been consumed in its formation. These experiments were followed by other oxidation experiments, in which burning was shown to be a combination with a gas and not the destruction of matter as previously supposed. Lavoisier's work not only established oxygen as a new and important element and illuminated the nature of burning or combustion, it also verified the law of conservation of mass since combustion reactions were shown to obey it. This inspired further quantitative work from which came the rest of the laws of combination and the Atomic Theory in the early part of the nineteenth century.

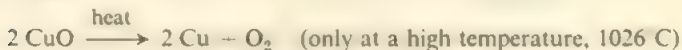
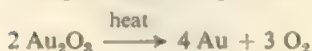
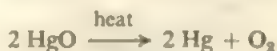


## 4. PREPARATION OF OXYGEN GAS

Oxygen may be prepared by several different methods. The most obvious method is to heat compounds containing oxygen, as was done by Priestley, Scheele and Lavoisier.

A. CERTAIN BINARY COMPOUNDS OF OXYGEN (OXIDES)  
LOSE ALL THEIR OXYGEN WHEN HEATED

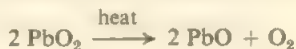
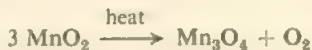
Among these are mercuric oxide, gold oxide, silver oxide, and copper oxide.



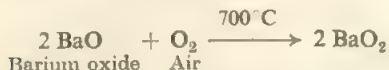
Notice that in the Periodic Table these elements fall in the transition series in between the periods of 8. Although the diagonal relationship of electronegativity does not hold within the transition group, it does place the entire group as metals with great attraction for electrons. These metals have sufficient attraction for electrons to pull their normal valence electrons from oxygen when heated and thus return to the metallic or elemental state. The alkali and alkaline earth metals could never attract electrons from an oxide ion. The four elements listed above, whose oxides can be completely decomposed upon heating, will be shown later to be less reactive in other respects.

B. OTHER BINARY COMPOUNDS OF OXYGEN (OXIDES) LOSE  
ONLY PART OF THE OXYGEN THEY CONTAIN WHEN HEATED

Among these oxides are manganese dioxide, lead dioxide and barium peroxide:



The last reaction was, at one time, the second step in a cycle to prepare oxygen from air on a commercial basis. First barium oxide was heated in the presence of air to  $700^\circ\text{C}$ , at which temperature the oxygen combined with it to form barium peroxide:



The  $\text{BaO}_2$  was then heated in a vacuum; oxygen was released as shown in the

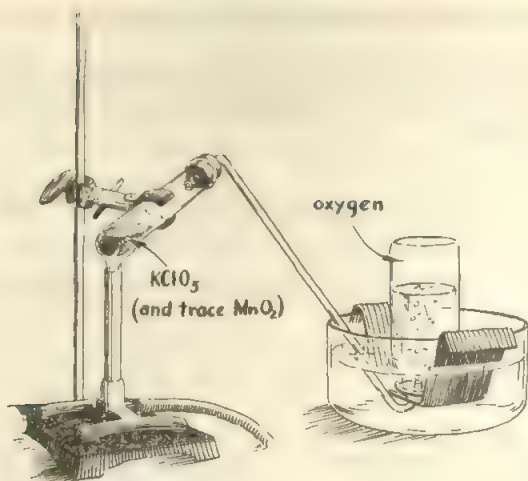


Figure 11.3. Preparation of oxygen.

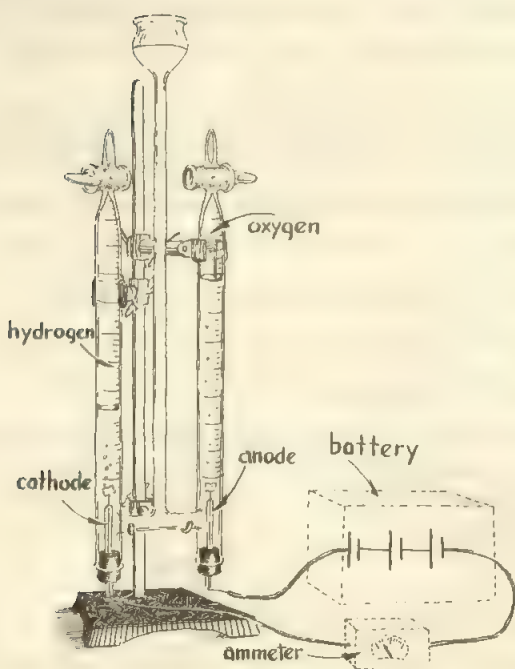
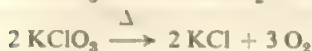
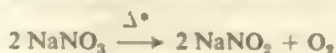


Figure 11.4. Electrolysis of water.

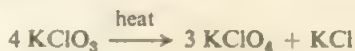
equation above. The same barium oxide was used again and again. Cheaper methods have now replaced this novel cycle.

### C. CERTAIN OTHER COMPOUNDS RELEASE ALL OR PART OF THEIR OXYGEN WHEN HEATED

Among these compounds are sodium nitrate and potassium chlorate.



Under proper conditions, the second reaction represents a convenient and often used method for making oxygen in the laboratory. When heated alone, potassium chlorate decomposes slowly at 400°C, not at lower temperatures. At the same time it decomposes slowly by another process forming potassium perchlorate.



However, when a trace of manganese dioxide is added, decomposition to give oxygen occurs very rapidly at 200°C, much below the temperature required to form the perchlorate. At 200°C, manganese dioxide contributes no oxygen and is found as manganese dioxide in the potassium chloride when all the potassium chlorate has been decomposed. The strange ability of certain materials, called catalysts, to hasten chemical reactions without being consumed is often not understood, but it is used extensively in industry. Much research is occupied with the search for proper catalysts. A convenient apparatus for producing oxygen and collecting it in the laboratory is shown in Figure 11.3.

### D. SODIUM PEROXIDE LOSES OXYGEN WHEN WATER IS ADDED



As shown in the equation, heat is released along with oxygen. When a few drops of water are added to a mixture of sawdust and sodium peroxide, the heat liberated is sufficient to ignite the sawdust, which burns brightly in the atmosphere of escaping oxygen.

### E. OXYGEN MAY BE PREPARED ALONG WITH HYDROGEN BY ELECTROLYSIS OF WATER

A trace of either a base or an acid must be added to conduct the electric current through the water, for water is a non-conductor. Water is then decomposed by electrical energy into its components: hydrogen and oxygen.

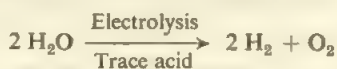


Figure 11.4 shows a demonstration cell for the electrolysis of water. The

\*  $\Delta$  signifies heat.

apparatus is filled with a very dilute solution of sulfuric acid. Leads from platinum electrodes are sealed through the glass walls of the electrolysis cell and connected to the positive and negative poles of a storage battery, as indicated by the signs on the drawing. When the circuit is closed, bubbles rise from each electrode and a gas collects in each tube. The gas collects at a faster rate above the negative electrode, at exactly double the rate in the other. This gas burns in air, forming water. It is hydrogen. The gas collected above the positive electrode supports combustion; it is oxygen. Some oxygen and hydrogen are produced commercially today at isolated power plants when electric power is plentiful and cheap.

#### F. AIR IS THE IMPORTANT COMMERCIAL SOURCE OF OXYGEN

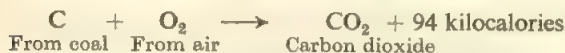
The method consists primarily in separating oxygen from nitrogen. This is done in much the same way that alcohol is separated from water, and gasoline is separated from fuel oil—by distillation. Alcohol is more volatile (boils at a lower temperature) than water. When the mixture is distilled, the vapor is richer in alcohol. By repeated distillation in an ingenious apparatus called a distillation column, the two liquids can be separated. Nitrogen boils at a lower temperature ( $-195^{\circ}\text{C}$ ) than oxygen ( $-183^{\circ}\text{C}$ ). They can be separated by the same fractional distillation process described for water, and alcohol. However, the mixture is a gas and must be liquefied first. This is done by cooling the gas under pressure. This process is the principal source of oxygen and nitrogen, both of which are used in great quantities.

### 5. THE REACTIONS AND USES OF OXYGEN

The many uses of oxygen depend upon the ease with which oxygen combines with many materials. Rapid combination accompanied with a flame is known as burning or combustion. Slower combination is known simply as oxidation; but the term may describe both types of combination.

#### A. OXYGEN IS OFTEN USED FROM AIR

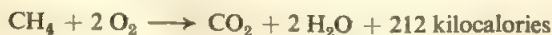
When coal burns, the major reaction is the combustion of carbon,



or, if insufficient oxygen is present, carbon monoxide is formed:

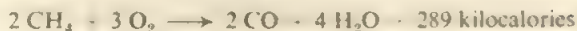


Natural gas, mostly methane,  $\text{CH}_4$ , burns with oxygen with three possible sets of products, depending on the amount of oxygen present. The three reactions may take place simultaneously. This reaction occurs when plenty of oxygen is present:

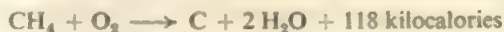




With less oxygen present, this is the major reaction:



and with still less oxygen:

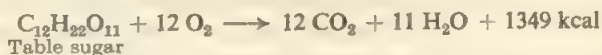


A luminous flame occurs when little oxygen is present, because flakes of carbon remain and are heated to incandescence in the flame. A sooty flame is yellow, because the carbon particles glow with a yellow light in the heat of the flame.

The heat value has been added to the equation because it is the important result of the reaction. A kilocalorie (kcal) is 1000 calories. When 1 mole of carbon (12 grams) is completely oxidized to  $\text{CO}_2$ , 94,000 calories of heat are liberated. When 2 moles (24 grams) of carbon are oxidized to CO, 52,800 calories are released. One can see that it is important economically for a furnace to have a sufficient draft.

Reactions like those above that give off heat are called *exothermic reactions*. Certain reactions are *endothermic*, that is, heat is absorbed during the reaction. All furnaces use oxygen from the air to combine with the fuel (coal, gas, or fuel oil), liberating carbon oxides, water vapor and heat. In an automobile engine, oxygen of the air supports the explosion of gasoline vapors in the cylinders to push the piston down.

Oxygen in inhaled air is carried to the cells to oxidize carbohydrates for energy and body heat. The products of the oxidation of sugar in the body cells:



are the same products obtained when sugar is completely burned in a flame.

## B. OXYGEN IS ALSO USED IN PURIFIED OR ENRICHED FORM

Various torches pre-mix oxygen and a combustible gas for a hotter flame. Oxygen and natural gas are used in a glass blower's torch:



A hotter flame is obtained with an oxygen-hydrogen mixture.



The oxyacetylene torch mixes oxygen and acetylene prior to burning and gives a flame reaching  $2800^\circ\text{C}$ , sufficiently hot to melt steel and to patch it by melting welding rod steel into breaks. The reaction is represented by this equation:



Air enriched with oxygen is often administered to people who have some types of lung congestions, or to people who suffer difficulty in breathing.

## C. COMBUSTION

Since the most important uses of oxygen involve combustion and since many tragedies result from uncontrolled combustion, the factors that affect it merit discussion.

1. *Proper mixing* of the reactants (oxygen and the combustible material), intimately and in the right proportions, aids combustion. For this reason the gaseous fuel and oxygen are mixed in an acetylene torch. Reactions cannot occur unless the reactants contact each other, molecule for molecule. Air and gasoline vapor are mixed in the carburetor to give fast, even burning in the automobile cylinder. Explosions in flour mills result only when powdered flour gets mixed up or dispersed through the air. Even aluminum dust will explode if blown into air in the right proportions and ignited.
2. An *increase in concentration* of either reactant, oxygen or combustible material, with the elimination of inert materials, aids combustion. An oxygen-acetylene mixture burns much more rapidly and hotter than an air-acetylene mixture, because the gases are in better contact and there is no unreactive nitrogen to be heated. Rocket fuel mixtures use liquid oxygen to get a higher concentration.
3. Combustion proceeds more rapidly at *higher temperatures*. Substances will not burn below the kindling temperature. Acetylene will not burn in oxygen at room temperature. It must be heated above that temperature with a match or a spark to start it. The flame spreads as the gases are heated. Spontaneous combustion illustrates the importance of temperature. Suppose an easily oxidized substance such as an oil is absorbed in a pile of rags. It begins to oxidize slowly in air, producing heat which escapes too slowly through the rags. The temperature rises and the oxidation proceeds faster giving more heat until the kindling temperature is reached and the rags burst into flame. Many a haystack has burned because damp hay began to rot (oxidize), producing sufficient heat to raise an area above kindling temperature.
4. *Oxidation (not combustion)* is aided in the body by catalysts. Enzymes in the body catalyze the oxidation of foodstuffs so that they can be oxidized rapidly at body temperature far below the kindling temperature. We have much to learn about these body catalysts.

D. COMPARISON OF THE REACTION OF OXYGEN WITH  
REPRESENTATIVE MEMBERS OF THE PERIODIC TABLE  
(ESPECIALLY THE METALS) IS INTERESTING

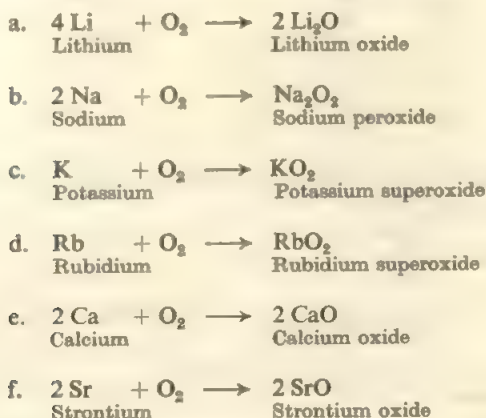
Oxygen forms normal oxides (binary compounds containing the simple oxide ion) with most elements. Examples using a period of seven elements are shown (Table 11.4). Sodium, with a valence of  $+1$ ; Mg, with a valence of  $+2$ ; Al, with a valence of  $+3$  have the normal oxide. This is also the case with the remaining oxides, although in those the bonding is covalent, and the

term "normal" oxide has little significance. Though the metals do exhibit normal oxides, they may not be the oxides gained on direct combination of the elements.

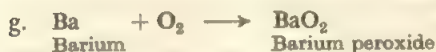
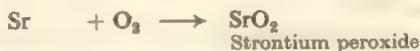
**Table 11.4. Some Representative Oxides**

Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub> P <sub>2</sub> O <sub>3</sub>	SO <sub>3</sub> SO <sub>2</sub>	Cl <sub>2</sub> O
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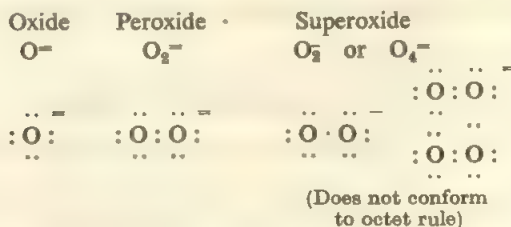
Equations illustrating the direct combination of oxygen with certain of the alkali and alkaline earth metals are shown below.



and some:



All these compounds are ionic. The following ions must exist, with these possible electronic structures:



If we were to classify these metals into three groups according to the products they form with oxygen, those forming superoxides would be most

active, followed by those forming peroxides. The seven elements listed would be grouped in decreasing activity in this manner:

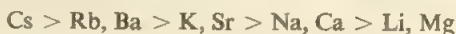


This order of reactivity based on only one type of reaction is in fairly good agreement with that predicted by the position of the elements in the Periodic Table, a portion of which is reproduced in Table 11.5. The diagonal relation-

**Table 11.5. Position of Alkali and Alkaline Earth Metals in the Periodic Table**

H		
<u>Li</u>	<u>Be</u>	
<u>Na</u>	<u>Mg</u>	
<u>K</u>	<u>Ca</u>	Sc
<u>Rb</u>	<u>Sr</u>	Y
<u>Cs</u>	<u>Ba</u>	La

ship, based on electronegativity and ionization potential, indicates the following order of decreasing activity.



### EXERCISES

- Judging from the position of oxygen in the Periodic Table:
  - Is it a metal or a non-metal?
  - What is its ionic valence?
  - What is its electronegativity comparative to its neighbors?
  - Is it more reactive than sulfur?
- Name all the elements that are gases at room temperature. In what general portion of the Periodic Table are they found?
- Why is chlorine a gas at room temperature and bromine not?
  - Why is radon a gas and bromine not?
- Compare the densities, melting points, boiling points and chemical reactivities of oxygen ( $\text{O}_2$ ) and ozone ( $\text{O}_3$ ).
- Why should oxygen gas be less soluble in water than hydrogen chloride gas?
- List in order the five most abundant elements in the earth's crust.
- Write balanced equations for the preparation of oxygen from: (a)  $\text{HgO}$ , (b)  $\text{Au}_2\text{O}_3$ , (c)  $\text{NaNO}_3$ , (d)  $\text{KClO}_3$ , (e)  $\text{Na}_2\text{O}_2$ .
- Describe the reaction conditions for the laboratory preparation of oxygen from potassium chlorate.
- What is a catalyst? Give an example of catalysis.
- Describe the major commercial method for the preparation of oxygen.
- What might one do to speed up the rate of combustion of two reactants?
- Explain how spontaneous combustion occurs.
- Why should the flame from a oxy-hydrogen torch be hotter than that of hydrogen burning in air?
- Write balanced equations for the burning of each of the following: lithium, sodium, and cesium. What do they indicate about the relative chemical activity of the three metals?
- Where are the active metals found in the Periodic Table?
- Write valence electron structures (dot formulas) for: oxygen gas, sodium peroxide, sodium monoxide, ozone and sulfur dioxide.



## PROBLEMS

Balance each of the following equations. If necessary refer to directions in Chapter 5.

1.  $\text{HgO} \longrightarrow \text{Hg} + \text{O}_2$
2.  $\text{Ag}_2\text{O} \longrightarrow \text{Ag} + \text{O}_2$
3.  $\text{Au}_2\text{O}_3 \longrightarrow \text{Au} + \text{O}_2$
4.  $\text{MnO}_2 \longrightarrow \text{Mn}_2\text{O}_3 + \text{O}_2$
5.  $\text{KClO}_3 \xrightarrow{\text{catalyst}} \text{KCl} + \text{O}_2$
6.  $\text{KClO}_3 \longrightarrow \text{KClO}_4 + \text{KCl}$
7.  $\text{BaO} + \text{O}_2 \longrightarrow \text{BaO}_2$
8.  $\text{NaNO}_3 \longrightarrow \text{NaNO}_2 + \text{O}_2$
9.  $\text{H}_2 + \text{O}_2 \longrightarrow \text{H}_2\text{O}$
10.  $\text{CH}_4 + \text{O}_2 \longrightarrow \text{CO}_2 + \text{H}_2\text{O}$
11.  $\text{CH}_4 + \text{O}_2 \longrightarrow \text{CO} + \text{H}_2\text{O}$
12.  $\text{CH}_4 + \text{O}_2 \longrightarrow \text{C} + \text{H}_2\text{O}$
13.  $\text{C}_2\text{H}_4 + \text{O}_2 \longrightarrow \text{CO}_2 + \text{H}_2\text{O}$
14.  $\text{C}_2\text{H}_{10} + \text{O}_2 \longrightarrow \text{CO} + \text{H}_2\text{O}$
15.  $\text{CuO} + \text{H}_2 \longrightarrow \text{H}_2\text{O} + \text{Cu}$
16.  $\text{Cu} + \text{Ag}_2\text{SO}_4 \longrightarrow \text{CuSO}_4 + \text{Ag}$
17.  $\text{Fe}_2\text{O}_3 + \text{CO} \longrightarrow \text{Fe} + \text{CO}_2$
18.  $\text{Fe} + \text{H}_2\text{O} \longrightarrow \text{Fe}_2\text{O}_3 + \text{H}_2$
19.  $\text{CS}_2 + \text{O}_2 \longrightarrow \text{CO}_2 + \text{SO}_2$
20.  $\text{H}_2\text{S} + \text{O}_2 \longrightarrow \text{H}_2\text{O} + \text{SO}_2$
21.  $\text{Cu} + \text{S} \longrightarrow \text{Cu}_2\text{S}$
22.  $\text{Na}_2\text{O}_2 + \text{H}_2\text{O} \longrightarrow \text{NaOH} + \text{O}_2$
23.  $\text{Ag}_2\text{O} + \text{H}_2\text{O}_2 \longrightarrow \text{Ag} + \text{O}_2 + \text{H}_2\text{O}$
24.  $\text{N}_2 + \text{H}_2 \longrightarrow \text{NH}_3$
25.  $\text{Mg} + \text{O}_2 \longrightarrow \text{MgO}$
26.  $\text{Mg} + \text{N}_2 \longrightarrow \text{Mg}_3\text{N}_2$
27.  $\text{PBr}_3 + \text{H}_2\text{O} \longrightarrow \text{H}_3\text{PO}_3 + \text{HBr}$
28.  $\text{NaOH} + \text{HCl} \longrightarrow \text{NaCl} + \text{H}_2\text{O}$
29.  $\text{Ca(OH)}_2 + \text{HCl} \longrightarrow \text{CaCl}_2 + \text{H}_2\text{O}$
30.  $\text{H}_2\text{S} + \text{NH}_3 \longrightarrow (\text{NH}_4)_2\text{S}$
31.  $\text{H}_2\text{S} + \text{NaOH} \longrightarrow \text{Na}_2\text{S} + \text{H}_2\text{O}$
32.  $\text{HCl} + \text{NH}_3 \longrightarrow \text{NH}_4\text{Cl}$
33.  $\text{AgNO}_3 + \text{NaCl} \longrightarrow \text{AgCl} + \text{NaNO}_3$
34.  $\text{BaCl}_2 + \text{Na}_2\text{SO}_4 \longrightarrow \text{BaSO}_4 + \text{NaCl}$

35.  $\text{Cu}(\text{NO}_3)_2 + \text{H}_2\text{S} \longrightarrow \text{CuS} + \text{HNO}_3$   
36.  $\text{Ca}(\text{HCO}_3)_2 \longrightarrow \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2$   
37.  $\text{Cl}_2 + \text{NaBr} \longrightarrow \text{Br}_2 + \text{NaCl}$   
38.  $\text{AgCl} + \text{NH}_3 \longrightarrow \text{Ag}(\text{NH}_3)_2\text{Cl}$   
39.  $\text{Br}_2 + \text{NH}_4\text{I} \longrightarrow \text{NH}_4\text{Br} + \text{I}_2$   
40.  $\text{F}_2 + \text{H}_2\text{O} \longrightarrow \text{HF} + \text{O}_2$   
41.  $\text{Na} + \text{H}_2\text{O} \longrightarrow \text{NaOH} + \text{H}_2$   
42.  $\text{Zn} + \text{Cu}(\text{NO}_3)_2 \longrightarrow \text{Zn}(\text{NO}_3)_2 + \text{Cu}$   
43.  $\text{Al} + \text{CuCl}_2 \longrightarrow \text{AlCl}_3 + \text{Cu}$   
44.  $\text{Ba}(\text{OH})_2 + \text{Na}_2\text{SO}_4 \longrightarrow \text{BaSO}_4 + \text{NaOH}$   
45.  $\text{HNO}_3 + \text{Ba}(\text{OH})_2 \longrightarrow \text{Ba}(\text{NO}_3)_2 + \text{H}_2\text{O}$   
46.  $\text{HI} + \text{H}_2\text{SO}_4 \longrightarrow \text{H}_2\text{O} + \text{H}_2\text{S} + \text{I}_2$   
47.  $\text{KOCI} \longrightarrow \text{KClO}_3 + \text{KCl}$   
48.  $\text{Cl}_2 + \text{KOH} \longrightarrow \text{H}_2\text{O} + \text{KCl} + \text{KOCI}$   
49.  $\text{Sb}_2\text{S}_3 + \text{Fe} \longrightarrow \text{FeS} + \text{Sb}$   
50.  $\text{As}_4\text{S}_6 + \text{O}_2 \longrightarrow \text{As}_4\text{O}_6 + \text{SO}_2$

# CHAPTER 12

## HYDROGEN

### 1. HISTORY OF THE DISCOVERY OF HYDROGEN

References to the preparation of hydrogen appear early in scientific history. In the beginning of the Revival of Learning following the Dark Ages, when chemistry was being born from alchemy, Paracelsus (1493–1541), a “practicer of medicine,” is believed to have observed a gas evolved when metals were treated with acids. Van Helmont, a Belgian physician of the next century (1577–1644), apparently knew of the same gas, and in the seventeenth century, Robert Boyle, whose gas law we have studied, both prepared and isolated hydrogen.

However, it remained for the shy, eccentric Englishman, Henry Cavendish (1731–1810), to characterize the gas and thus gain recognition for its discovery. In 1766, Cavendish published a paper describing his preparation of “inflammable air” and discussing its properties. He had prepared the gas in the usual way by treating a metal with acid. It is obvious that he had burned it. Because hydrogen would not support combustion, he identified it with phlogiston. In 1783, eleven years after Scheele’s discovery of oxygen and six years after Lavoisier announced the modern theory of combustion, Cavendish combined hydrogen and oxygen and obtained water.

It was upon this experiment that Lavoisier named the new gas “hydro-gen,” water-former. Cavendish clung to the phlogiston theory and never recognized that in burning, hydrogen had combined with oxygen.

### 2. OCCURRENCE OF HYDROGEN

Hydrogen is very widely distributed in nature, being found in water and almost all compounds that are or were constituents of living things. It is

estimated that 16% of all the atoms of the earth's crust (atmosphere, plants, animals, oceans and a 10-mile shell) are hydrogen atoms. But, because the hydrogen atom is so light (the lightest of all elements), less than 1% of the earth's crust (by weight) is hydrogen.

### 3. PREPARATION AND PRODUCTION OF HYDROGEN

Hydrogen is prepared by a variety of methods:

A. One method is that employed by Cavendish and those who preceded him: the *reaction of a metal with an acid*. Zinc reacts with either dilute

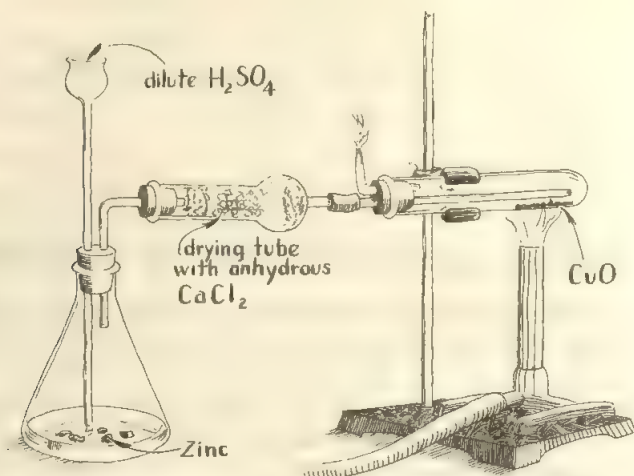
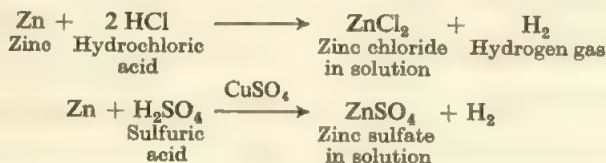


Figure 12.1. Hydrogen generator.

sulfuric acid or dilute hydrochloric acid as represented by the following equations:



This reaction usually proceeds nicely; however, it may be accelerated by the addition of a little copper sulfate solution. A laboratory assembly for the preparation of hydrogen is shown in Figure 12.1. All connections must be airtight to prevent loss of the gas and to minimize possibility of a fire.

Mossy zinc, used because of its large surface area, is placed in the Erlenmeyer flask. After replacing the stopper, dilute sulfuric acid is added through the thistle tube. The acid solution covers the metal, starting the reaction. The end of the thistle tube is covered by the acid, preventing the escape of hydrogen. The hydrogen gas passes through a loose plug of cotton where any acid spray



is collected, then over anhydrous calcium chloride where it is dried of water vapor by this reaction:



Many anhydrous substances have a great attraction for water. Anhydrous calcium chloride combines with the water absorbed to form a dihydrate.

The dried hydrogen passes into the large test tube, sweeping the air before it, then out the glass tip. *After all the air has been expelled*, the stream of hydrogen issuing from the tip may be lighted and observed to burn.

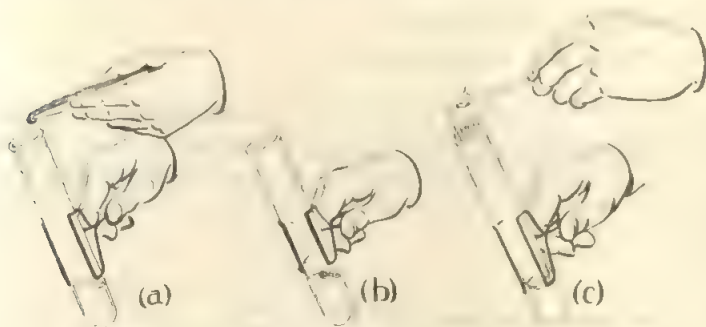
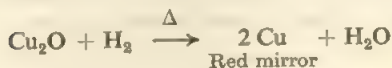
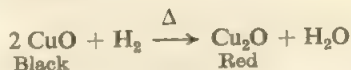


Figure 12.2. Sodium on water.

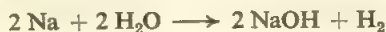
Cupric oxide was placed in the large test tube to illustrate a chemical property of hydrogen—its ability to reduce certain hot metal oxides. When heated in a stream of hydrogen, the black cupric oxide powder turns red and eventually becomes a metallic mirror on the inside surface of the test tube by these reactions:



The flame at the glass tip is extinguished when the escaping hydrogen is replaced by water vapor from these reactions.

B. *Some metals react with water to produce hydrogen.* When a piece of sodium is dropped into a test tube with a small quantity of water (Fig. 12.2a, b), it skips about at random on the surface. Close observation reveals that gas bubbles are forming and bursting at a rapid rate between the metal and the water. This causes the metal to move about.

The gas liberated in the bubbling is flammable and explodes with air when ignited (Fig. 12.2c). It is hydrogen. Lye water is left in the test tube. This reaction occurs:



It is more difficult to free hydrogen from water than from acids, for all metals that will react with water will react with explosive violence with dilute acids. These are called active metals. Table 12.1 is a partial list of some

**Table 12.1. Partial Activity Series**

<div style="display: inline-block; vertical-align: middle;"> <div style="border: 1px solid black; padding: 2px; text-align: center;">K</div> <div style="border: 1px solid black; padding: 2px; text-align: center;">Ba</div> <div style="border: 1px solid black; padding: 2px; text-align: center;">Ca</div> <div style="border: 1px solid black; padding: 2px; text-align: center;">Na</div> </div>	}	Will replace $H_2$ from cold water $Ba + 2 H_2O \rightarrow Ba(OH)_2 + H_2$	}	*React explosively with acids $Ca + 2 HCl \rightarrow CaCl_2 + H_2$
<div style="border: 1px solid black; padding: 2px; text-align: center;">Mg</div>	}	Will react with boiling water $Mg + 2 H_2O \rightarrow Mg(OH)_2 + H_2$	}	
<div style="border: 1px solid black; padding: 2px; text-align: center;">Al</div> <div style="border: 1px solid black; padding: 2px; text-align: center;">Mn</div> <div style="border: 1px solid black; padding: 2px; text-align: center;">Zn</div> <div style="border: 1px solid black; padding: 2px; text-align: center;">Fe</div> <div style="border: 1px solid black; padding: 2px; text-align: center;">Cd</div> <div style="border: 1px solid black; padding: 2px; text-align: center;">Ni</div>	}	Will react with steam when "red hot" $3 Fe + 4 H_2O \rightarrow Fe_3O_4 + 4 H_2$	}	React vigorously with acids to give $H_2$ $Mg + 2 HCl \rightarrow MgCl_2 + H_2$
<div style="border: 1px solid black; padding: 2px; text-align: center;">Sn</div> <div style="border: 1px solid black; padding: 2px; text-align: center;">Pb</div>	}	No reaction with either water or steam	}	Very slow reaction with acids
<div style="border: 1px solid black; padding: 2px; text-align: center;">Cu</div> <div style="border: 1px solid black; padding: 2px; text-align: center;">Hg</div> <div style="border: 1px solid black; padding: 2px; text-align: center;">Ag</div> <div style="border: 1px solid black; padding: 2px; text-align: center;">Au</div> <div style="border: 1px solid black; padding: 2px; text-align: center;">Pt</div>	}	No reaction with water	}	Will not react with acids

common metals in order of decreasing activity for yielding hydrogen. It is called the *activity series*. The metals that will react with both acids and water and those that react only with acids are indicated.

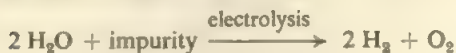
The positions of the metals listed in this partial activity series are shown in the Periodic Table (Table 12.2). Notice that those metals sufficiently active to react with cold water (K, Ba, Ca and Na) are in the lower left-hand corner. Those that react actively with acids (Mg, Al, Mn, Zn, Cr and Fe), but which react with water only under strenuous conditions are either among or near the transition elements; the metals that react poorly with acids or that do *not* react with acid or water are at the right of the transition elements. It might be

\* The acid solution contains 1 mole per liter.



Carbon dioxide is removed as before. Other hydrocarbons, methane ( $\text{CH}_4$ ), ethane ( $\text{C}_2\text{H}_6$ ), ethylene ( $\text{C}_2\text{H}_4$ ), etc., are used. Great tonnages of hydrogen are used each year. It is shipped under high pressure in steel tanks.

- E. *Hydrogen like oxygen may be prepared by electrolysis of water.* A certain amount is produced for commercial purposes in areas where electric power is cheap.



- F. *Calcium hydride and lithium hydride pills* were a portable source of hydrogen for inflating observation balloons during war time. They were kept in specially sealed, water tight, packages. On addition of water the metallic hydrides are decomposed giving hydrogen.



The balloon was attached to a little metal container, water was poured into the container, the hydride pill dropped in, the container closed. The hydrogen formed inflated the balloon.

#### 4. HYDROGEN AND THE PERIODIC TABLE

The electronic structure and the position of hydrogen in the Periodic Table were discussed in Chapter 7. Part of that discussion may be repeated and expanded here with profit.

Hydrogen is element number 1. It contains only 1 electron and possesses a nucleus of 1 proton. Because of this, the hydrogen atom is the smallest of all atoms. At STP the density of hydrogen gas is equal to  $(2.016 \text{ g}/22.4 \text{ L} =) 0.0898 \text{ g/L}$ . Next in density comes helium, a monatomic gas having a density of  $(4.003 \text{ g}/22.4 \text{ L} =) 0.178 \text{ g/L}$ .

Hydrogen gas is much lighter than air and will rise in air. Therefore, hydrogen issuing from a generator can be collected with a test tube held upside down. The hydrogen rises in the tube, forcing the air out. A balloon filled with hydrogen gas will rise in air. Additional weight can be added and the balloon will rise if the sum of the weights of the balloon, the added mass and the hydrogen is less than the weight of the volume of air the balloon displaces.

Air has an average molecular weight of 29 (being  $4/5$  nitrogen and  $1/5$  oxygen), and a density of  $1.299 \text{ g/L}$  at STP. One liter of hydrogen will lift, in addition to its own weight,  $(1.299 \text{ g/L} - 0.0898 \text{ g/L} =) 1.21 \text{ g/L}$ . By the same reasoning, 1 liter of helium will lift  $(1.299 \text{ g/L} - 0.178 \text{ g/L} =) 1.12 \text{ g/L}$ .

Hydrogen has only one electron in its only and outer energy level, which has a capacity of two electrons. In that it has only one electron in the valence shell, it resembles the alkali metals. For this reason hydrogen is often placed above lithium in the Periodic Table. Unlike the alkali metals, hydrogen seldom, if ever, loses that one electron in a chemical reaction. With only one electron, a hydrogen atom need gain or share only one more to gain an inert



gas (helium) structure. It does this in all reactions. In this sense it is similar to the halogens (fluorine, chlorine, bromine and iodine). Often it is placed above fluorine in the table. While this position is probably preferable to the other, it is not completely satisfactory (Chapter 7).

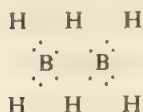
As mentioned above, hydrogen may contribute its one electron to share with an electron of another atom, forming a covalent bond, or it may gain an electron to form an ion. Binary compounds of hydrogen with the elements of the first two periods of eight in the table illustrate this. These are listed below (Table 12.3).

**Table 12.3. Some Binary Compounds of Hydrogen**

LiH	BeH <sub>2</sub>	B <sub>2</sub> H <sub>6</sub>	CH <sub>4</sub>	NH <sub>3</sub>	H <sub>2</sub> O	HF
Li <sup>+</sup> :H <sup>-</sup>	H: <sup>-</sup> Be <sup>++</sup> :H <sup>-</sup>	$  \begin{array}{ccccc}  & \text{H} & & \text{H} & \\  & \cdot & & \cdot & \\  & \text{B} & & \text{B} & \\  & \cdot & & \cdot & \\  & \text{H} & & \text{H} &   \end{array}  $	$  \begin{array}{c}  \text{H} \\  \cdot \\  \text{H}:\text{C}:\text{H} \\  \cdot \\  \text{H}  \end{array}  $	$  \begin{array}{c}  \text{H} \\  \cdot \\  :\text{N}:\text{H} \\  \cdot \\  \text{H}  \end{array}  $	$  \begin{array}{c}  \cdot \\  \text{H}:\text{O}: \\  \cdot \\  \text{H}  \end{array}  $	$  \begin{array}{c}  \cdot \\  \text{H}:\text{F}: \\  \cdot  \end{array}  $
NaH	MgH <sub>2</sub>	*(AlH <sub>3</sub> )	SiH <sub>4</sub>	PH <sub>3</sub>	H <sub>2</sub> S	HCl
Na <sup>+</sup> :H <sup>-</sup>	H: <sup>-</sup> Mg <sup>++</sup> :H <sup>-</sup>		$  \begin{array}{c}  \text{H} \\  \cdot \\  \text{H}:\text{Si}:\text{H} \\  \cdot \\  \text{H}  \end{array}  $	$  \begin{array}{c}  \text{H} \\  \cdot \\  :\text{P}:\text{H} \\  \cdot \\  \text{H}  \end{array}  $	$  \begin{array}{c}  \cdot \\  \text{H}:\text{S}: \\  \cdot \\  \text{H}  \end{array}  $	$  \begin{array}{c}  \cdot \\  \text{H}:\text{Cl}: \\  \cdot  \end{array}  $

Hydrogen forms ionic binary compounds with the metals of the first two groups of the Periodic Table. In these compounds hydrogen exists as the H<sup>-</sup> ion (called the hydride ion), having gained an electron, and exhibits the electron configuration of helium. These compounds are called hydrides. For example: CaH<sub>2</sub>, calcium hydride; NaH, sodium hydride. Hydrogen forms covalent bonds with the non-metals, gaining the two electron configuration by sharing. These covalent binary compounds of hydrogen are not generally called hydrides, but are known by common names: CH<sub>4</sub>, methane; NH<sub>3</sub>, ammonia; PH<sub>3</sub>, phosphine; H<sub>2</sub>O, water; etc. Apparently some binary compounds of the transition elements and hydrogen exist. However, they may be solid solutions of hydrogen in the metal rather than compounds.

Diborane, B<sub>2</sub>H<sub>6</sub>, written in the table as:



is an unstable compound, but it does exist. A summation of the available valence electrons reveals that the boron atoms cannot have an octet of electrons about each if the structure is as written. Diborane remains an exception to the octet rule.

\* AlH<sub>3</sub> is not known.

The existence of the hydride ion,  $\text{H}^-$ , in metal hydrides is demonstrated in the electrolysis of molten sodium hydride ( $\text{NaH}$ ; Fig. 12.3). Sodium appears as a lake around the negative electrode and hydrogen gas is liberated at the positive electrode.

Very seldom, and never in the presence of water, does hydrogen lose an electron to become an  $\text{H}^+$  ion. The ion we represent as  $\text{H}^+$  and call the hydro-

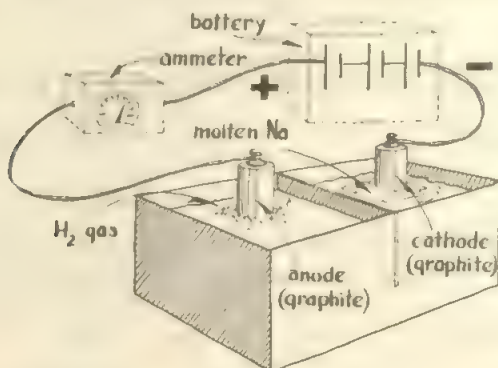
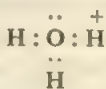


Figure 12.3. Electrolysis of molten sodium hydride.

gen ion, is more properly represented as  $\text{H}_2\text{O}\cdot\text{H}^+$  or  $\text{H}_3\text{O}^+$ , and is correctly called the hydronium ion. Its electron configuration is represented as:



The tendency of hydrogen atoms to gain electrons or to share them, but not to lose electrons might be expected from hydrogen's position in the electronegativity scale of atoms (see Chapter 7).

## 5. PROPERTIES OF HYDROGEN

Hydrogen is the least dense of all gases. It is odorless and colorless. It exists in diatomic, non-polar molecules with little attraction between them. Therefore, it boils at a very low temperature ( $20.38^\circ\text{A}$ ) and freezes at a still lower temperature ( $13.92^\circ\text{A}$ ). It is a flammable gas, burning quietly when emitted from a jet in air, but exploding with violence when ignited in an air mixture.

## 6. ISOTOPES OF HYDROGEN

Hydrogen atoms come in three sizes (masses). The three are listed on page 167 with a summary of properties, names and occurrences.

The per cent of deuterium in hydrogen is so small as to make no perceptible difference in the atomic weight, although the isotope is nearly twice as heavy as light hydrogen. Nevertheless, considerable amounts of deuterium were

Table 12.4. Hydrogen Isotopes

	Mass	% of Natural Hydrogen	Boiling Point	Freezing Point
Hydrogen ${}^1\text{H}$ light hydrogen	1.008	99.9844	$-253^\circ\text{C}$	$-259^\circ\text{C}$
Deuterium ${}^2\text{H}$ heavy hydrogen	2.0146	0.0156	$-249^\circ\text{C}$	$-254.6^\circ\text{C}$
Tritium ${}^3\text{H}$		$10^{-12}$ to $10^{-10}$		

isolated from water for use in the atomic bomb. Hydrogen is the only element having isotopes with so great a mass ratio as 2 to 1. There is more difference between the properties of hydrogen and deuterium, because of this fact, than between isotopes of any other element. The freezing and boiling points of heavy hydrogen are approximately three degrees greater than for ordinary hydrogen. The two can be separated by repeated distillations.

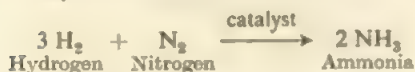
In general, deuterium reacts with the same chemicals that ordinary hydrogen does, forming similar compounds. Heavy water,  $\text{D}_2\text{O}$ , is an example. Sometimes in reactions, compounds containing heavy hydrogen are used to identify the role of that hydrogen in the reaction. However, deuterium is usually less reactive and reacts more slowly than ordinary hydrogen. Tritium is produced by nuclear transformations. Its occurrence in nature is very small. It is formed from the action of cosmic rays on some nuclei. It is radioactive and gradually decays like radium. This accounts for its scarcity. Deuterium and tritium are involved in the fusion mechanism of the so-called hydrogen bomb.

## 7. USES AND REACTIONS OF HYDROGEN

### A. HYDROGENATION

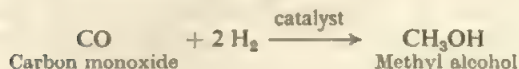
The most important commercial use of hydrogen is in the production of other valuable chemicals by a process called hydrogenation.

- (1) *Ammonia is produced by hydrogenating nitrogen gas in the presence of a catalyst.*



Ammonia is used as a base in chemical processes. It is the major raw material for the production of nitric acid and for many fertilizers.

- (2) *Methyl alcohol (wood alcohol) is produced by combining carbon monoxide and hydrogen:*



- (3) *Coal releases hydrocarbons when hydrogen is passed over it in the presence of a catalyst.*

- (4) *Vegetable oils are hardened by combination with hydrogen to make margarine and other kinds of shortening.*

### B. HYDROGEN IS USED IN WELDING

- (1) In the *hydrogen-oxygen torch*, the two gases are mixed and burn together at a high temperature as they emerge from the tip (Fig. 12.4). Objects may be heated in any oxy-hydrogen flame to about 2800°C.

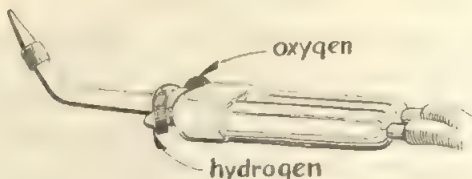


Figure 12.4. Oxy-hydrogen torch.

- (2) An interesting method of obtaining high temperatures is shown in the *atomic hydrogen torch* (Fig. 12.5). A great quantity of energy is required to split a hydrogen molecule into atoms.

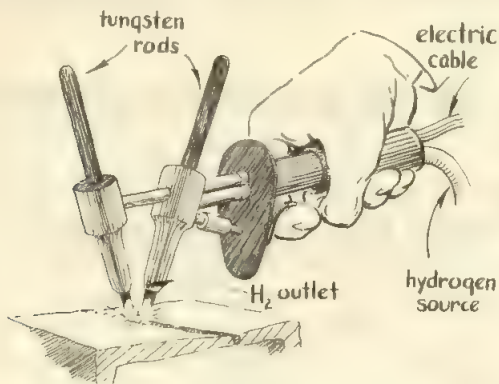
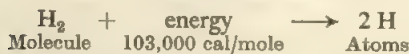


Figure 12.5. Atomic hydrogen torch.

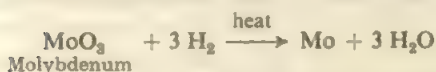
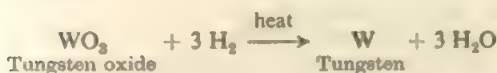
Upon recombination the energy is released. This recombination is catalyzed by a metal surface. In the atomic hydrogen torch, hydrogen gas is passed between two sparking electrodes. Electrical energy from the arc splits the molecules into atoms. When the stream of atoms hits the metal surface, they pair together, liberating that large quantity of heat. The hydrogen then burns with air, liberating more calories. The



temperature of the flame is about 5000°C and can be used to melt most metals.

### C. HYDROGEN IS USED IN THE COMMERCIAL PRODUCTION OF SOME METALS

Earlier in the chapter, an experiment was described in which hot cupric oxide was reduced to copper metal in a stream of hydrogen. *Hydrogen will reduce the hot oxides of metals of intermediate activity.* In general all oxides of the metals between iron and copper in the activity series (p. 162) can be reduced by this method. Oxides of the metals below copper can be reduced merely by heating while oxides of those above iron are stable even in the presence of hydrogen at high temperature. Two metals, tungsten and molybdenum, are prepared commercially by reduction with heat and hydrogen.



### D. HYDROGEN IS USED TO EQUIP LIGHTER-THAN-AIR CRAFT

The lifting power of hydrogen gas in air has been discussed in another section. Hydrogen is used to fill weather balloons. It has been used to fill lighter-than-air craft, dirigibles and balloons, especially in Germany between the two World Wars. Several tragedies resulted because of the extreme flammability of hydrogen in air. Because of this, unreactive helium, with nearly as much lifting power, has replaced hydrogen.

## 8. THE MOST IMPORTANT COMPOUND CONTAINING HYDROGEN IS WATER

### A. STRUCTURE OF WATER

*Water is probably the most important of all compounds.* The structure of the molecule gives the compound many physical and chemical properties that enhance its utility.

The water molecule whose formula is  $\text{H}_2\text{O}$  contains two hydrogen atoms, each bound by sharing of electrons to a central oxygen atom. One might assume the molecule to be symmetrical, with the oxygen atom in the center and the hydrogen atoms on each side. This is not true. The water molecule is bent (Fig. 12.6), with the angle between the two OH bonds being approximately 104°. Because the three atoms do not lie in a straight line and because

oxygen is much more electronegative than hydrogen, the water molecule is highly polar. The direction of polarity is shown in Figure 12.6.

Because of this polarity, water molecules have a great attraction for one another and they tend to "line-up" plus ends to minus ends. Great energy is required to pull them apart, as evidenced by the melting point,  $0^{\circ}\text{C}$ , and the

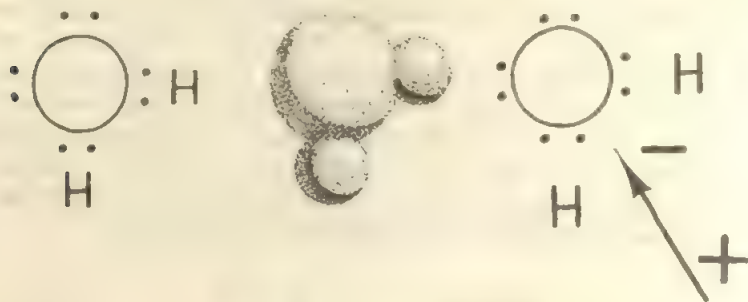


Figure 12.6. The water molecule.

boiling point,  $100^{\circ}\text{C}$ , which are exceptionally high for a substance of such low molecular weight.

### B. SOME USES OF WATER

Water molecules also have a great attraction for other polar molecules and for ions, and therefore water is a good solvent for ionic and polar compounds. Water is the solvent in soil, plant and animal chemistry. Salts are leached from the soil by water, carried into the plant and the cells, where they combine with water and carbon dioxide to become the "minerals." Without sufficient water to carry nutrients, plant cells starve and the plant wilts. Digestion in animals occurs with the aid of acids in water solution. The products of digestion are carried in water solution in the blood to the cells, where they are oxidized in water in the cell to give body heat and energy. Many reactions of ionic substances occur only in water solution. *Water is the most important of all solvents.*

### C. PROPERTIES OF WATER

Most liquids increase in density when cooled. The decrease in molecular motion allows the molecules to crowd more closely together. Further, most liquids contract on freezing as the translational motion ceases and the molecules freeze tightly together. This is not true for water; the V-shaped molecules, in packing positive end to negative end, pack more loosely than they might if they could "fold" together. When water is cooled, it contracts, and the density increases until  $4^{\circ}\text{C}$  is reached. At that point, the trend reverses and water expands slowly. At  $0^{\circ}\text{C}$  the water freezes with a further expansion. It is believed that the increase in volume in cooling from  $4^{\circ}\text{C}$  to  $0^{\circ}\text{C}$  is due to an increasing partial orienting of the molecules—positive end

to negative end. The complete orienting of the molecules occasions an abrupt expansion upon freezing.

This unusual property of water (expansion upon freezing) is "both a blessing and a curse." The tremendous pressure exerted when water freezes is sufficient to break iron pipes and steel automobile engine heads. But rocks are reduced to soil by the freezing of water in cracks. Solid granite blocks were split in early days by the freezing of water in plugged holes. When water freezes in lakes and streams, a scum forms on the surface, which thickens to a crust and eventually to a slab that may be several feet thick. In any case, freezing occurs at the underside of the ice layer. The ice already formed tends to insulate the water below since the heat must pass out through it. This retards the freezing and keeps the water below the ice from dropping below freezing. Were ice more dense than water so that it dropped to the bottom, lakes and streams would freeze more rapidly. Fish and other marine life in northern waters would not survive the winter.

#### D. PURIFICATION OF WATER

Although some appear to prefer other beverages, few will deny the importance of water in the home. It quenches our thirst. With the help of a little soap it keeps us, our clothes and the dishes clean. Perhaps the liberal use of soap and water has done more to reduce the incidence of diseases than has any other factor. But water must be pure or it may harbor agents of ill health. Water must be purified before it is fit for human consumption. The purification procedure varies with both the source, the state of the water supply and the use. At worst, *water may contain trash and silt, bacteria and chemicals* (usually dissolved salts). Very often, at the source it contains all three.

Water is purified in various ways:

1. Trash and silt are removed by filtration, often through a sand or gravel bed.
2. Bacteria are killed by the addition of chlorine gas. Often when bacteria are present in large numbers, as in the "spring run-off," so much chlorine is added that it can be tasted in the water. Other chemicals may also be used.
3. If the salts are injurious to health or react with the soap to form a scum, they may be removed by distillation of the water, an expensive process. Ion exchangers (tanks of materials which substitute harmless ions for unwanted ions) are often used.

#### EXERCISES

1. Which was discovered first, hydrogen or oxygen?
2. What does the word hydrogen mean?
3. How is it that 16% of all atoms on the earth's crust are hydrogen atoms, but only 1% by weight is hydrogen?
4. How many elements (see Table 11.3) have more atoms in the earth's crust than does hydrogen?

5. Name five metals that may be used with an acid to produce hydrogen.
6. Name two catalysts mentioned in the last two chapters and tell where they are used.
7. Is pure hydrogen explosive? Explain.
8. List these gases in the order of increasing density (at STP): oxygen, air, hydrogen and helium.
9. Write equations for the reduction of  $\text{Fe}_3\text{O}_4$ ,  $\text{CuO}$ ,  $\text{MoO}_3$  and  $\text{WO}_3$  to their respective metals.
10. List four metals that will react with cold water to produce hydrogen. In what area of the Periodic Table do these metals appear?
11. Write equations for six different methods of preparing hydrogen.
12. How much additional weight can be lifted by 20 liters of hydrogen at STP in air? The average molecular weight of air is 29. How much additional weight may be lifted by a 20 liter helium balloon at STP?
13. Write dot formulas (valence electron structures) for the binary hydrogen compounds of the elements lithium to fluorine in the Periodic Table.
14. What is unusual about the electron structure of diborane?
15. Write valence electron structures for: (a) the hydride ion, (b) the hydronium ion, (c) the hydroxide ion, (d) the water molecule.
16. Give the names and relative masses of the three hydrogen isotopes.
17. List three industrial uses of hydrogen gas. Which is the major use?
18. Describe the operation of: (a) the oxy-hydrogen torch, (b) the atomic hydrogen torch.
19. State three physical properties of water that stem in part from the polarity of the water molecules. Explain the relationship.
20. Why is it advantageous that water expands on freezing?
21. List the three steps in the purification of contaminated water.



# CHAPTER 13

## QUANTITATIVE RELATIONSHIPS IN CHEMICAL PROCESSES

It is obvious that quantitative relationships among raw materials and between raw materials and products are of utmost importance to chemical industries. Industrial leaders need to know the exact proportions of raw materials required to make the product and must know the amount of each of these raw materials necessary to produce a given quantity of product. The economic feasibility of a process depends primarily on the amount and cost of raw materials, the amount and price of products, and the cost of transforming the raw materials into products.

A chemical process may depend upon one or several chemical reactions. If only one chemical reaction is involved, one need simply find relationships among reactants (raw materials) and between reactants and products. If the process involves a group of reactions, one must solve the quantitative problem for each reaction and finally combine them for the whole process. In either case, the problem involves quantitative relationships for one reaction.

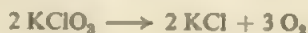
There are two aspects to the problem of quantities in a chemical reaction. (1) there is a *theoretical* or a 100% relationship based upon the Law of Conservation of Mass and the assumption that all of the reactant will be converted to products. This can be calculated. It is the purpose of this chapter to describe those calculations. (2) However, reactions seldom do give the theoretical yield. One rarely gains 100% of the product possible, because reactions stop before the reactants are used up. Often "side-reactions" occur (the chemicals react in another way simultaneously to produce a second, unwanted set of products).

Some of the products are lost in purification. The per cent of the theoretical amount one may obtain cannot be calculated for a reaction. One might

"carry-out" a "trial-run" under the conditions used in the process to determine this. In any case, the yield will not be greater than the theoretical (100% possible). Great sums of money are spent in industrial research to find better reaction conditions, conditions under which the yield of products will more nearly approach 100%.

### MOLE RELATIONSHIPS AMONG REACTANTS AND PRODUCTS

To calculate the theoretical, or 100% relationships among reactants and products, one needs the equation for the reaction. The equation must be balanced. As stated before, a balanced equation is a shorthand statement of the law of conservation of mass for a given reaction. Consider the equation for the thermal decomposition of potassium chlorate in the presence of a trace of manganese dioxide:



The balanced equation indicates the source and disposition of all atoms involved. This agrees with the fact that atoms are neither gained nor lost in a chemical reaction.

The equation may be applied to the decomposition of any amount of potassium chlorate:

1. In the trivial and hypothetical case of the decomposition of 2 molecules of potassium chlorate, the equation indicates that upon decomposition: 2 "molecules" of  $\text{KClO}_3$  yields two "molecules" of  $\text{KCl}$  and 3 molecules of  $\text{O}_2$ .
2. In general terms, potassium chlorate decomposes into potassium chloride and oxygen in the molecular ratio: 2 to 2 to 3, respectively.
3. In terms of numbers of gram-molecular weights or moles for the trivial case, the decomposition of 2 moles, the equation reads:

2 moles of  $\text{KClO}_3$  yields 2 moles  $\text{KCl}$  and 3 moles of  $\text{O}_2$

4. In general terms, potassium chlorate decomposes into potassium chloride and oxygen in the ratio:

2 moles of  $\text{KClO}_3$  to 2 moles  $\text{KCl}$  to 3 moles  $\text{O}_2$

Thus,

- a. When 1 mole of  $\text{KClO}_3$  decomposes,

1 mole of  $\text{KCl}$  and  $3/2$  moles  $\text{O}_2$  are formed.

- b. When 1 mole of oxygen is prepared,

$2/3$  mole  $\text{KClO}_3$  disappears and  $2/3$  mole  $\text{KCl}$  appears.

- c. When 0.505 mole  $\text{KClO}_3$  is decomposed,

0.505 mole  $\text{KCl}$  and  $0.505 \times 3/2$  mole = 0.757 mole of  $\text{O}_2$  are formed.

The equation for the preparation of hydrogen gas by reaction of white hot iron with steam may be used to illustrate mole relationships.



#### EXAMPLES:

1. How many moles of  $\text{Fe}_3\text{O}_4$  can be produced by reaction of 1 mole of Fe?

$$1 \text{ mole Fe} \times \frac{1 \text{ mole Fe}_3\text{O}_4}{3 \text{ mole Fe}} = 1/3 \text{ mole Fe}_3\text{O}_4$$

2. How many moles of steam ( $\text{H}_2\text{O}$ ) react with 0.462 mole Fe?

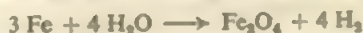
$$0.462 \text{ mole Fe} \times \frac{4 \text{ moles H}_2\text{O}}{3 \text{ moles Fe}} = 0.615 \text{ mole H}_2\text{O}$$

3. How many moles of iron are consumed in the preparation of 0.25 mole  $\text{H}_2$ ?

$$0.25 \text{ mole H}_2 \times \frac{3 \text{ moles Fe}}{4 \text{ moles H}_2} = 0.188 \text{ mole Fe}$$

#### WEIGHT RELATIONSHIPS AMONG REACTANTS AND PRODUCTS

By using atomic and molecular weights, one can readily transfer mole relationships into weight relationships. The product of the number of moles of a sample and its molecular weight is the weight in grams. The quotient of weight of a sample divided by the molecular weight gives the number of moles in the sample. Examples of these calculations appear below. They refer to the same process for producing hydrogen gas and to the same equation:



#### EXAMPLES:

1. How many g of iron must react to produce 0.25 mole  $\text{H}_2$ ? One step is added beyond the previous calculations:

$$0.25 \text{ mole H}_2 \times \frac{3 \text{ moles Fe}}{4 \text{ moles H}_2} = 0.188 \text{ mole Fe}$$

and 0.188 mole Fe is:

$$0.188 \text{ mole Fe} \times \frac{56 \text{ g Fe}}{\text{mole Fe}} = 10.5 \text{ g Fe}$$

(56 is the approximate atomic weight of iron; the more exact value is 55.85.)

The setup in full is:

$$0.25 \text{ mole H}_2 \times \frac{3 \text{ moles Fe}}{4 \text{ moles H}_2} \times 56 \text{ g Fe/mole Fe} = 10.5 \text{ g Fe}$$

2. What weight of white-hot iron will react with 4.0 g of steam?

The molecular weight of water is  $2 \times 1.0 + 16 = 18$ . One mole of water is 18 g.

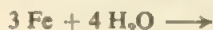
4 g of  $\text{H}_2\text{O}$  is:

$$\frac{4 \text{ g}}{18 \text{ g/mole}} = 4/18 \text{ mole}$$

4/18 mole of  $\text{H}_2\text{O}$  reacts with:

$$4/18 \text{ mole } \text{H}_2\text{O} \times \frac{3 \text{ moles Fe}}{4 \text{ moles } \text{H}_2\text{O}} = 1/6 \text{ mole Fe}$$

(The fraction 3/4 is from this portion of the equation.)



And 1/6 mole Fe is:

$$1/6 \text{ mole Fe} \times 56 \text{ g Fe/mole Fe} = 9.27 \text{ g Fe}$$

The complete setup is:

$$\frac{4 \text{ g}}{18 \text{ g/mole}} \times 3/4 \times 56 \text{ g/mole} = 9.27 \text{ g}$$

3. How many g  $\text{Fe}_3\text{O}_4$  are produced along with 7.25 g of  $\text{H}_2$ ? There are:

$$\frac{7.25 \text{ g}}{2 \text{ g/mole}} = 3.63 \text{ moles of } \text{H}_2$$

From the relevant portion of the balanced equation ( $\rightarrow \text{Fe}_3\text{O}_4 + 4 \text{ H}_2$ ), the moles of iron oxide produced are:

$$3.63 \text{ moles } \text{H}_2 \times \frac{1 \text{ mole } \text{Fe}_3\text{O}_4}{4 \text{ moles } \text{H}_2} = 0.908 \text{ mole } \text{Fe}_3\text{O}_4$$

Because 1 mole of  $\text{Fe}_3\text{O}_4$  is  $(3 \times 56) + (4 \times 16) \text{ g} = 232$ ,

$$0.908 \text{ mole } \text{Fe}_3\text{O}_4 \times 232 \text{ g } \text{Fe}_3\text{O}_4/\text{mole } \text{Fe}_3\text{O}_4 = 211 \text{ g } \text{Fe}_3\text{O}_4$$

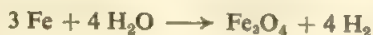
The setup is:

$$\frac{7.25 \text{ g}}{2 \text{ g/mole}} \times 1/4 \times 232 \text{ g/mole} = 211 \text{ g } \text{Fe}_3\text{O}_4$$

### VOLUME RELATIONSHIPS AMONG REACTANTS AND PRODUCTS

By using molecular weights one can calculate weight relationships among reactants and products. In the same general way, volume relationships may be calculated by using molecular volumes (volume per mole). For solids and liquids the mole volume may be found by dividing the molecular weight by the density (which is recorded in tables). However, these calculations are not so important generally as volume calculations with gases. Gas volume calculations (of both reactants and products) are simplified by the fact that all gases have the same mole volume at STP—22.4 liters. STP volumes are involved in the calculations below.

EXAMPLE 1. In this example the same equation will be used as was used above:





1. How many liters of hydrogen gas at STP may be prepared from reaction of steam with 40 g of Fe?

Beginning as before, the moles of  $H_2$  produced will be:

$$\frac{40 \text{ g}}{56 \text{ g/mole}} \times 4/3 = 0.952 \text{ mole } H_2$$

But a mole of any gas is 22.4 L at STP, and the volume of the 0.952 mole  $H_2$  is:

$$0.952 \text{ mole} \times 22.4 \text{ L/mole} = 21.3 \text{ L at STP}$$

The complete setup for the problem is:

$$\frac{40 \text{ g}}{56 \text{ g/mole}} \times 4/3 \times 22.4 \text{ L/mole} = 21.3 \text{ L at STP}$$

2. How many g of steam ( $H_2O$ ) is consumed in producing 10 L of hydrogen gas at STP?

The moles of hydrogen produced are:

$$\frac{10 \text{ L}}{22.4 \text{ L/mole}} = 0.446 \text{ mole}$$

This would then require:

$$\frac{10}{22.4} \text{ mole} \times 4/4 \times 18 \text{ g/mole} = 8.03 \text{ g water}$$

One must correct the volume at STP if desired for any other conditions.

3. How many liters of hydrogen gas measured at  $150^\circ\text{C}$  and 640 mm may be prepared from the reaction of 40 g of iron with steam?

At STP the volume is:

$$\frac{40 \text{ g}}{56 \text{ g/mole}} \times 4/3 \times 22.4 \text{ L/mole} = 21.3 \text{ L at STP}$$

At  $150^\circ\text{C}$  ( $423^\circ\text{A}$ ) and 640 mm the volume of this gas sample is:

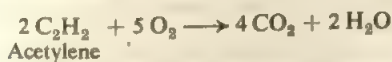
$$21.3 \text{ L} \times \frac{423^\circ\text{A}}{273^\circ\text{A}} \times \frac{760 \text{ mm}}{640 \text{ mm}} = 39.2 \text{ L}$$

The complete setup is:

$$\frac{40 \text{ g}}{56 \text{ g/mole}} \times 4/3 \times 22.4 \text{ L/mole} \times \frac{423^\circ\text{A}}{273^\circ\text{A}} \times \frac{760 \text{ mm}}{640 \text{ mm}} = 39.2 \text{ L}$$

## EXAMPLE 2

Volume to volume calculations can be made by the same method. Acetylene burns with oxygen according to the following equation:



How many liters of  $\text{CO}_2$  at 640 mm and  $25^\circ\text{C}$  are produced when 15 L of acetylene at  $25^\circ\text{C}$  and 640 mm are burned?

$$\frac{15 \text{ L} \times \frac{640 \text{ mm}}{760 \text{ mm}} \times \frac{273^\circ\text{A}}{298^\circ\text{A}}}{22.4 \text{ L/mole}} \times 4/2 \times 22.4 \text{ L/mole} \times \frac{760 \text{ mm}}{640 \text{ mm}} \times \frac{298^\circ\text{A}}{273^\circ\text{A}} = 30 \text{ L}$$

Notice that all figures in the mathematical equation will cancel except 4, 2, the mole ratio in the equation and 15 L.

$$15 \text{ L} \times 4/2 = 30 \text{ liter of CO}_2$$

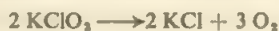
This simplification reminds one of Avogadro's Hypothesis: "Equal volumes of gas at the same temperature and pressure contain an equal number of molecules." Therefore, since there are twice the number of  $\text{CO}_2$  molecules formed, the volume of  $\text{CO}_2$  is double the volume of the acetylene burned.

## PROBLEMS

Atomic weights: C = 12; Fe = 56; K = 39; Pb = 208; Cl = 35.5; H = 1.0; Mn = 55; S = 32.

Equations for reactions involved in Problems 3, 4, and 7-10.

I. Preparation of oxygen from potassium chlorate



II. Reduction of iron oxide with carbon monoxide



III. Preparation of hydrogen by passing steam over molten iron



IV. Oxidation of lead sulfide with hydrogen peroxide



V. Preparation of oxygen by thermal decomposition of manganese dioxide



VI. Complete combustion of methane



VII. Incomplete combustion of methane



VIII. Complete combustion of carbon disulfide



1. How many moles (or what fraction of a mole) is:

(a) 100 g  $\text{KClO}_3$ , (b) 35 g Fe, (c) 10 g CO, (d) 74 g PbS, (e) 56 g  $\text{Mn}_3\text{O}_4$ , (f) 106 g  $\text{CO}_2$ , (g) 25 g  $\text{CH}_4$ , (h) 36 g  $\text{SO}_2$ ?

2. What is the weight of one mole of:

(a) KCl, (b)  $\text{O}_2$ , (c)  $\text{H}_2$ , (d)  $\text{H}_2\text{O}$ , (e) Fe, (f)  $\text{H}_2\text{O}_2$ , (g)  $\text{MnO}_2$ , (h)  $\text{CH}_4$ , (i)  $\text{CS}_2$ ?

3. Use equations above.

a. How many moles of  $\text{O}_2$  are produced with decomposition of 1 mole  $\text{KClO}_3$ ?

b. How many moles of hydrogen are gained by the reaction of 1 mole of iron with steam? By the reaction of 0.625 mole of Fe?

c. How many moles of water will react with 1 mole of Fe? With 0.625 mole of Fe?

d. How many moles of iron are produced by reaction of 1 mole of CO with  $\text{Fe}_3\text{O}_4$ ? By reaction of 0.32 mole of CO?

e. How many moles of  $\text{H}_2\text{O}_2$  react with 1 mole of PbS? With 0.308 mole?

f. How many moles of  $\text{MnO}_2$  are needed to produce 1 mole of  $\text{Mn}_3\text{O}_4$ ? To produce 0.244 mole of  $\text{Mn}_3\text{O}_4$ ?

g. How many moles of oxygen combine with  $\text{CH}_4$  to produce 1 mole of  $\text{CO}_2$ ? To produce 2.41 moles of  $\text{CO}_2$ ?

- h. How many moles of  $O_2$  combine with 1 mole of  $CH_4$  to give  $CO$ ? Combine with 1.56 moles of  $CH_4$ ?
- i. How many moles of oxygen are required to produce 1 mole of  $SO_2$  in the complete combustion of carbon disulfide? To produce 0.563 mole of  $SO_2$ ?
4. a. How many g of  $KCl$  are produced upon the decomposition of 100 g of  $KClO_3$ ? How many g of  $O_2$ ?
- b. How many g of hydrogen gas are produced by reaction of 35 g of red hot iron with steam?
- c. How many g of iron may be produced by reaction of 10 g of  $CO$  with  $Fe_2O_3$ ?
- d. How many g of  $H_2O_2$  will react with 74 g of lead sulfide to produce  $PbSO_4$ ?
- e. How many g of  $MnO_2$  must be decomposed to gain 56 g of  $Mn_2O_3$ ?
- f. How much oxygen is consumed in the complete burning of a sample of methane if 106 g of  $CO_2$  are obtained?
- g. How much oxygen is consumed in burning 25 g of  $CH_4$  when the products are  $CO$  and  $H_2O$ ?
- h. 36 g of sulfur dioxide were produced by the burning of carbon disulfide. How much oxygen was consumed?
5. What is the volume of (a) 1 mole of  $O_2$  at STP, (b) 1 mole of  $CH_4$  at STP, (c) 1 mole of  $CO_2$  at 760 mm and  $-63^\circ C$ , (d) 2 moles of  $CH_4$  at  $150^\circ C$  and 600 mm, (e) 0.564 mole  $H_2$  at 3 atm and  $273^\circ C$ ?
6. How many moles is (a) 3 L of  $O_2$  at STP, (b) 1 L of  $CO_2$  at STP, (c) 14 liters of  $CH_4$  at 760 mm and  $25^\circ C$ , (d) 37 L of  $CO$  at  $187^\circ C$  and 2.5 atm, (e) 15.5 L of  $SO_2$  at  $25^\circ C$  and 640 mm?
7. (a) How many liters of  $O_2$  at STP may be produced upon the decomposition of 100 g of  $KClO_3$ ? (b) How many liters of oxygen at 2 atm and  $150^\circ C$ ?
8. (a) What volume of hydrogen at STP is evolved when 35 g of white-hot iron react with steam? (b) What volume at  $25^\circ C$  and 640 mm?
9. (a) How many liters of  $CO_2$  at STP are produced when 10 L of  $CO$  at STP react with iron oxide? (b) How many liters of  $CO_2$  at 640 mm and  $125^\circ C$  are produced when 10 L of  $CO$  at 640 mm and  $25^\circ C$  reacts with iron oxide?
10. (a) How many g of  $Fe$  are produced when 15 L of  $CO$  measured at 890 mm and  $27^\circ C$  reacts with  $Fe_2O_3$ ? (b) How many liters of  $CO_2$  at STP are produced?

# CHAPTER 14

## THE ACTIVE METALS— Li, Na, K, Rb, Cs, Ca, Ba and Sr

### 1. PROPERTIES OF METALS IN GENERAL

Everyone is acquainted with the common metals iron, aluminum, gold and silver. These and all other metals possess certain remarkable properties that distinguish them from other solids. These properties vary from metal to metal, but they are, nevertheless, distinctive.

Table 14.1. The Metals

H																	Non-Metals					He
<div>Li</div> Be																	B	C	N	O	F	Ne
<div>Na</div> Mg	Metals																Al	<div>Si</div>	P	S	Cl	Ar
<div>K</div> <div>Ca</div>	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	<div>Ge</div>	As	Se	Br	Kr						
<div>Rb</div> <div>Sr</div>	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	<div>Sb</div>	Te	I	Xe						
<div>Cs</div> <div>Ba</div>	La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn						
<div>Fr</div> <div>Ra</div>	Ac																					
<div>Lw</div>																						

### A. PHYSICAL PROPERTIES

1. *Metals are hard*, not so hard as salts, but harder than crystals of covalent molecules. The hardness varies from soft sodium and lead to hard iron, tungsten and nickel.



2. *Metals have tensile strength.* Iron strands of a cable support heavy loads. Electrical transmission lines of copper and aluminum withstand the whipping of stiff winds without breaking.
3. *Metals are elastic.* A metal twisted, stretched or bent with a heavy load tends to return to its original shape when the load is lifted.

The action of all types of metal springs depends upon this property.

*Nevertheless:*

4. *Metals are malleable.* Hard iron may be hammered into thin strips. Although it is hard and resists deformation, the hammered metal is as hard as before. This property varies from metal to metal. Gold, which can be hammered into sheets so thin as to be transparent, is certainly more malleable than lead or iron.
5. *Metals are ductile.* When metal strands are strained beyond their tensile strength, they may be drawn into long, thin wires. Copper wire and iron wire are made by drawing the respective metal bars to many times their length. The resulting wire still possesses tensile strength.
6. *Metals possess a so-called metallic sheen.* All metals, except yellow gold and copper, have a silvery appearance. The shiny appearance is due to a near-total reflection of light. A thin coating of either silver or aluminum returns the light from the back surface of a mirror.
7. *Metals are good conductors of electricity and heat.* Metal cooking pots have wooden or plastic handles. Metal handles would be too hot to hold. The best conductors of electricity are silver, copper and aluminum, in that order. Other metals present a greater resistance to the flow of an electric current, but none is classed as a nonconductor.

*Alloys (solid mixtures, or compounds of metals with metals)* are, in general, poorer conductors of heat and electricity than the pure metals. Alloys are more rigid and less malleable and ductile than pure metals. Stainless steel cooking pots have either copper covered bottoms to spread the heat evenly or a laminated, sandwich-type construction with a better conductor between the non-tarnishing alloy layers. The iron-carbon alloy, cast iron, is noted for its brittleness.

## B. METALLIC BONDING

Bonds between atoms in a metal must use only those electrons available and must be consistent with the properties discussed above.

It is inconceivable that the bonding be ionic. One could not imagine one atom drawing electrons completely away from another identical atom. Such a structure is untenable with the properties of metals. Were metal bonds ionic, they would be brittle and could admit of neither malleability nor ductility.

There is an insufficient number of valence electrons to permit the formation of covalent molecules. Furthermore, the non-polar molecules would not hold together with sufficient force to give the tensile strength observed. Continuous covalent bonding through the crystal is impossible also, because

there are so few available electrons. Were the bond a continuous covalent network, deformation of the metal would require the making and breaking of many bonds.

Metallic bonding is neither ionic nor of the conventional covalent type. It seems that the metal is a lattice work of the metal ions packed as closely together as possible. The ions are held together by the valence electrons which occupy the interstices (spaces) between the ions in the crystal. The electrons are probably paired but occupy delocalized orbitals, that is, orbitals about many or all the ions in the crystal.

The properties of ductility and malleability are possible, for ions of a metal are piled like marbles in a box. Deformation of the metal merely changes the shape of the pile of ions. The ions in the pile are still as close to one another as before, and strength is maintained. The loosely bound electrons may be forced by an electric potential through the network of interstices to give an electric current.

Alloying may decrease the electrical conductivity and make the metal more brittle. Atoms of carbon are so small as to fit in the interstices in an iron crystal. In ordinary steel (carbon steel) carbon atoms with their 4 available electrons wedge themselves in between the iron atoms and share electrons with them. A partial covalent bond network is built up through the crystal tying up the electrons and making the metal more rigid.

### C. CHEMICAL PROPERTIES

In a chemical sense metals are characterized (as discussed in Chapter 7) by a relatively small attraction for electrons in the valence shell. As a consequence, in the typical reaction the atom loses an electron (or electrons) to become a positive ion. The relative attraction for electrons varies from metal to metal and has been predicted from the position of the metal in the Periodic Table. Those with the least attraction are the most active of metals.

## 2. THE ACTIVE METALS

The elements lithium, sodium, potassium, rubidium, cesium, calcium, strontium and barium have been mentioned as a group in each of two previous chapters. In both cases they were cited for exceptional chemical reactivity: (1) They combine directly and rapidly with oxygen in the air to form oxides, peroxides and superoxides. (2) They react with cold water to produce hydrogen gas.

Some other less active metals react with air slowly, especially in the presence of moisture. The rusting of iron wire is one such reaction. The same metals may replace hydrogen from boiling water or steam and from cold, dilute acid solutions, but are obviously much less active than the group listed above.



or *Activity Series* in the order of decreasing reactivity with acid solutions (Table 14.3). It is probable that the order of reactivity with water is the same. For the present the numbers listed under "potential" may be understood as the relative ease with which the metal replaces hydrogen from a solution containing 1 mole of acid per liter. Metals with a high negative potential

**Table 14.3. Electromotive Series**

<i>Metal</i>	<i>Potential</i>
Cesium (Cs)	−3.02
Lithium (Li)	−3.02
Rubidium (Rb)	−2.99
Potassium (K)	−2.92
Barium (Ba)	−2.90
Strontium (Sr)	−2.89
Calcium (Ca)	−2.87
Sodium (Na)	−2.71
Magnesium (Mg)	−2.34
Beryllium (Be)	−1.70
Aluminum (Al)	−1.67
Zinc (Zn)	−0.76
Chromium (Cr)	−0.71
Iron (Fe)	−0.44
Nickel (Ni)	−0.25
Tin (Sn)	−0.14
Lead (Pb)	−0.13
Hydrogen (H)	0.00
Copper (Cu)	+0.34
Mercury (Hg)	+0.80
Silver (Ag)	+0.80
Gold (Au)	+1.70

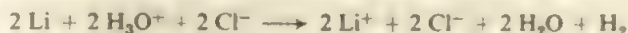
(−3.02 to −2.7) evolve hydrogen with explosive violence. Metals with intermediate values (−2.34 to −0.44) replace hydrogen at a reasonable rate. Metals with a still lower negative value react very slowly if at all. Metals with a positive value do not react. In fact, hydrogen gas at 1 atmosphere pressure may be absorbed in acid solutions of copper, silver or gold, causing them to be plated out.

The order of the active elements in the activity series: Cs, Li, Rb, K, Ba, Sr, Ca and Na is much as expected. Only lithium appears to be out of order. Lithium should occur last, after sodium, because of its greater electronegativity. One can understand the apparent contradiction only by realizing that the process involves more than the exchange of electrons. The reaction of lithium metal with dilute hydrochloric acid is represented by the equation:





The equation shows that lithium and hydrochloric acid react in the ratio of 2 gram-atomic weights (moles) to 2 moles, producing 1 mole of hydrogen gas for each 2 moles of lithium consumed. The ionic equation:

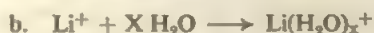


shows that hydrochloric acid solutions and lithium chloride solutions are ionic. The net ionic equation:



shows that lithium transfers an electron to the hydronium ion, releasing hydrogen from it.

The net ionic equation fails to show one fact. Lithium ions in solution are hydrated. That is, water molecules surround a lithium ion, with the negative end of their dipoles toward the positive ion. One of the free electron pairs of each water molecule may occupy the now vacant valence shell of the lithium. When a lithium ion is formed by losing an electron to a hydronium ion, it is hydrated at the same time.



Now, any one of the active metals will lose electrons to hydronium ions and with greater spontaneity than lithium, equation (a). Furthermore, all other metal ions become hydrated, but none so readily as lithium, equation (b), because of its small size and the possible close approach of the water molecules to the positive center. The spontaneity of this second step is so much greater for lithium than for all the rest, that when both steps occur simultaneously lithium has a greater potential than all the metals except cesium.

## B. PHYSICAL PROPERTIES OF THE ACTIVE METALS

Numerical values of some of the physical properties of the active metals are tabulated in Table 14.4; this will be referred to as needed.

**Table 14.4. Physical Properties of the Active Metals**

	Li	Na	K	Rb	Cs	Ca	Sr	Ba
Atomic Weight	6.929	22.990	39.102	85.47	132.905	40.08	87.62	137.34
Density at 20°C g/cm <sup>3</sup>	0.535	0.971	0.862	1.532	1.90	1.55	2.60	3.59
Melting Point, °C	179	97.9	63.5	39.0	28.5	851	800	850
Boiling Point, °C	1336	883	758	700	670	1487	1366	1537

The active metals have a metallic lustre resembling shiny silver. Often this is not apparent. For even when kept in oil to protect them from the oxygen and water vapor in the air, the metals become coated with a dull grey oxide. When the metals are cut, the shiny surface is visible, but it turns grey almost immediately. The alkali metals are soft and can be cut with a knife very easily. The alkaline earth metals in the group have somewhat the same softness as lead. All are good conductors of heat and electricity. Sodium is a

good conductor of both heat and electricity but its softness and its reactivity prevent its use as a conductor, except in special cases.

The low electronegativity might account for the electrical conduction. The outermost electrons are held very loosely and can easily be pushed from atom to atom by an electrical potential. The softness is probably related to this. If atoms had a great attraction for each others' electrons, the sharing of the electrons would hold the atoms together in a rigid crystalline structure. But the attraction is small, and the crystals are soft. The low densities, as shown in the table, are striking. The first three alkali metals are less dense than water; lithium is about one-half as dense as water. Because the atoms do not have great attraction for the valence electrons, they remain farther from the nucleus, and the atoms are larger. Also, the melting points are low (especially for the alkali metals). Cesium is a liquid above  $28^{\circ}\text{C}$ . This again appears to be due to a lack of attraction of the atoms for the electrons between them.

### C. OCCURRENCE OF THE ACTIVE METALS

Only three of the active metals, calcium, sodium and potassium, occur abundantly in nature. They constitute an average percentage of 3.63, 2.83 and 2.59 of igneous rock. Barium and strontium compounds are readily available in chemical houses because of the relatively high concentrations of the few deposits that do exist. Because of their great chemical reactivity, the elements are never found free in nature, but occur as the positive ion in salt deposits and in silicate minerals. Large deposits of sodium chloride are found in the remains of ancient inland seas. Salt occurs in a small percentage in ocean water, but constitutes up to as high as 25–27% of isolated inland seas such as the Great Salt Lake. These are the major sources of sodium. Good, usable deposits of potassium are rare. Potassium salts are often mixed with magnesium salts, chlorides or sulfates. This explains the high price and scarcity of potassium compounds. Calcium is often found as the carbonate,  $\text{CaCO}_3$ , in marble, chalk, limestone, coral and Iceland spar. It also occurs as the sulfate.

### D. PREPARATION OF THE ACTIVE METALS

Since an active metal always occurs in nature in ionic compounds, the preparation of the free metal involves the reduction of the metal ion to a metal atom. The electron or electrons lost in compound formation must be returned. But these elements are the least electronegative and cannot take electrons from other elements. Therefore, the metals are prepared electrolytically. Electrical energy is used to return the electrons to the metal ion.

Sodium is usually prepared by the electrolysis of fused sodium chloride. In an earlier chapter the electrolysis of salt was mentioned and diagrammed to aid in an understanding of ionic bonding. The Downs cell used for the commercial production of sodium will be described here. Fused sodium chloride with calcium chloride added to lower the melting temperature from  $800^{\circ}\text{C}$  to  $590^{\circ}\text{C}$  is electrolyzed in an iron pot lined with fire brick (Fig. 14.1).

A positive carbon electrode stands in the bottom, surrounded by a negative ring-shaped electrode. The electrodes are separated by a perforated steel divider, and a solid steel top covers the negative electrode. This serves to keep the products, chlorine gas and sodium, apart. Otherwise, they would combine again. At the surface of the negative electrode, sodium metal is formed:



The molten metal, being less dense than the chloride melt, floats to the top and spills over into a container. Chlorine gas forms above the anode (+ electrode) and is piped off to pressure tanks for shipping.

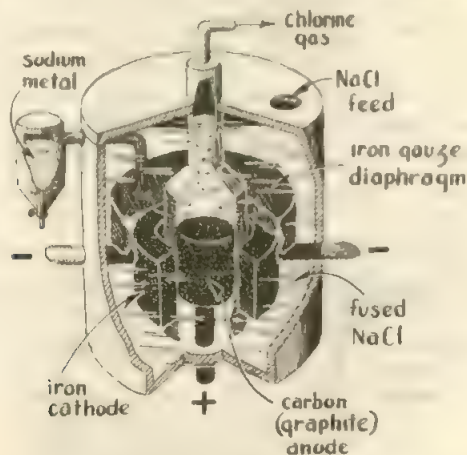
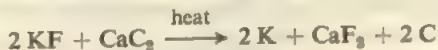


Figure 14.1. The Downs cell.

There is little demand for potassium. There are but few instances where cheaper sodium cannot be used instead of potassium. Potassium can be prepared in the same manner as sodium—by electrolysis of molten potassium chloride. Potassium is also obtained by heating potassium fluoride with calcium carbide to about  $1000^{\circ}\text{C}$  in steel cylinders.



Potassium is vaporized at this temperature and is collected by bubbling into hot paraffin.

Calcium is prepared by electrolyzing fused calcium chloride at  $800^{\circ}\text{C}$ , using a graphite anode and iron cathode. The electrolysis is started with the cathode just touching the surface of the liquid. As calcium forms on the electrode, it is raised slowly. A metallic rod of calcium forms as an extension. The calcium is broken off the cathode.

### E. USES OF SODIUM

Sodium metal is the only active metal used extensively in industry. The uses may depend on either chemical or physical properties. (1) A large

proportion of sodium (over 20,000 tons annually) is used in and is mixed with lead to form bricks of the alloy. The bricks are used in making tetraethyl lead, a gasoline additive. (2) Sodium is used as a catalyst in the production of numerous other organic compounds. (3) Some sodium metal is used for heat conduction. Molten sodium is poured into hollow valve stems of airplane engines. The sodium, molten at operating temperature, conducts the heat away from the valve head to prevent warping. (4) Sodium and other alkali metals are used in photoelectric light meter tubes.

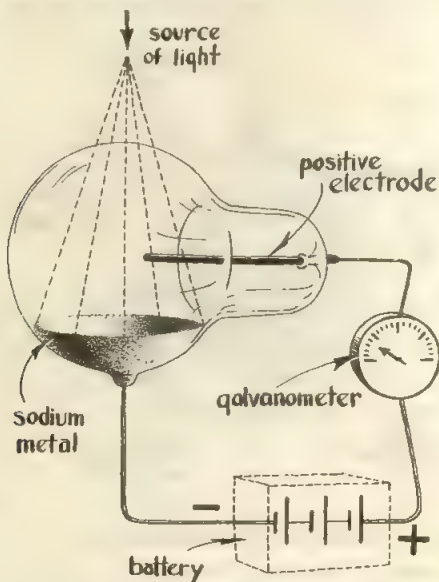


Figure 14.2. Light meter circuit (photoelectric cell).

A light meter circuit is shown in Figure 14.2. One side of the inner surface of a vacuum tube is coated with a fine film or mirror of sodium metal. The tube is so arranged in the meter that light may shine through the opposite side of the tube upon the sodium surface. The positive pole of the battery is connected through a galvanometer to a wire inside the vacuum tube.

The sodium mirror is connected to the negative pole of a battery. When no light falls upon the sodium surface (in the dark), no current flows through the galvanometer. When light shines on the surface, energy is absorbed, ejecting electrons. They are attracted to the positive electrode wire in the tube, completing the circuit and causing a current to flow. The number of electrons liberated, and therefore the current, is proportional to the light intensity.

(5) A small quantity of sodium is used in sodium vapor lamps. The characteristic yellow light is visible at greater distances on foggy nights.

#### F. COMPOUNDS OF THE ACTIVE METALS

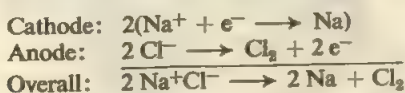
(1) *Potassium Compounds* are not used in great amounts. In almost all cases, the corresponding sodium compounds are just as suitable and are



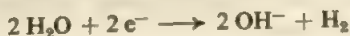
much cheaper. Potassium compounds are important in agriculture. Not less than 0.1% potassium in the soil is necessary for the healthy growth of the plants. The supply of potassium is continually being removed by the harvesting of crops and must be replenished. Some may be returned by adding plant and organic waste or ashes to the soil, but more may be added in chemical fertilizers in the form of potassium sulfate, potassium chloride or potassium nitrate. Potassium nitrate is found in deposits as a residue of the decay of animal matter. It is commonly called saltpeter, and is one of the components of black gunpowder; the other two are charcoal and sulfur.

- (2) *Sodium Compounds*: Several compounds of sodium are important commercially: sodium chloride ( $\text{NaCl}$ ), sodium hydroxide ( $\text{NaOH}$ ), sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), sodium bicarbonate ( $\text{NaHCO}_3$ ), and sodium sulfate ( $\text{Na}_2\text{SO}_4$ ). *Sodium chloride* is important as a seasoning for foods. Because of its availability in nature, it is the source of other sodium chemicals, for hydrochloric acid, and for sodium itself. The electrolysis of salt under various conditions illustrates both the use of salt and the preparation of some of these compounds.

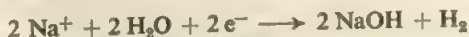
- (a) When *anhydrous salt* is melted and *electrolyzed*, sodium metal and chlorine gas are produced (Downs Cell; Fig. 14:1), the reactions occurring at the electrodes and the overall reaction being:



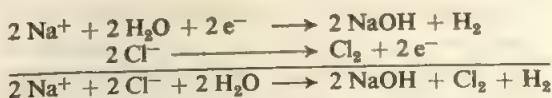
- (b) When *water* is added, making a *brine solution*, other products result, due to a change in the cathode reaction. Sodium metal cannot be prepared in the presence of water. If it were formed, sodium would react violently with water to give hydrogen gas and sodium hydroxide. Instead, however, water reacts at the cathode giving hydrogen and the hydroxide ion directly:



or, including the sodium ion:



The reaction at the anode is unchanged by the addition of water. The two electrode reactions are added here to give the overall reaction.



All three products are marketed. Sodium hydroxide is used in large quantities in industry. It is recovered from the solution. Hydrogen and chlorine are collected separately, compressed in tanks, and sold. Several million tons of chlorine are produced this

way every year, along with hydrogen gas for which there is a great demand in industry.

Various cells have been designed to produce sodium hydroxide, chlorine gas and hydrogen gas from brine. One of these is the Nelson cell (Fig. 14:3). The concentrated salt solution is held in a perforated

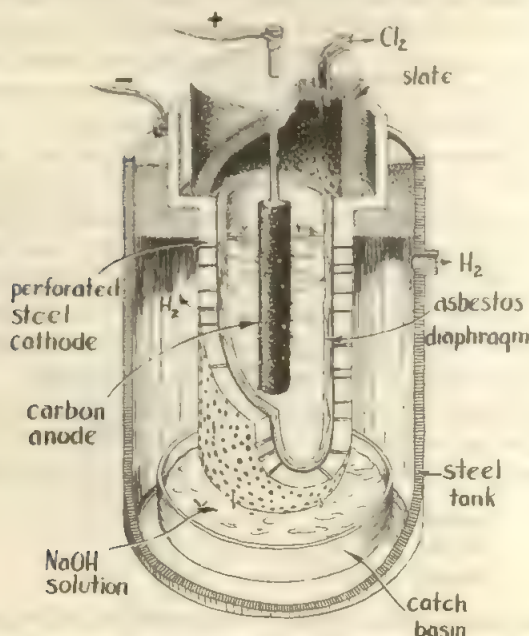
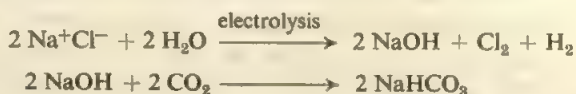


Figure 14.3. The Nelson cell.

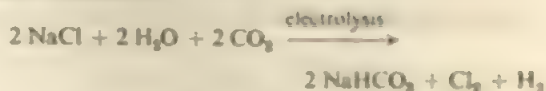
asbestos-lined steel container, which also serves as the cathode. A carbon anode is immersed in the solution. Chlorine is liberated at the anode and escapes through an outlet at the top to be compressed and stored.

Hydrogen gas is liberated from the solution as it passes through the cathode. The gas collects in a vessel about the thimble-shaped container and escapes through an outlet. The sodium hydroxide solution that remains drips steadily from the cathode into a catch basin. Chlorine gas comes in contact with neither the hydrogen nor the hydroxide solution.

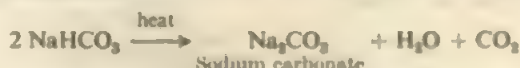
- (c) Addition of another gas, carbon dioxide ( $\text{CO}_2$ ), gives still other products. In operation  $\text{CO}_2$  may be bubbled into the cell during the electrolysis of brine. The carbon dioxide reacts with the sodium hydroxide formed to give  $\text{NaHCO}_3$ , sodium bicarbonate:



The overall reaction is:

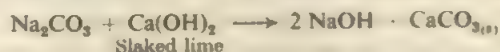


Again all three products are marketed. Sodium bicarbonate is baking soda. It is used medicinally and in baking powder, but the demand for it is not great. Most of the white salt is heated to form sodium carbonate:



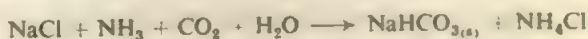
The carbon dioxide liberated in the heating is added to the carbon dioxide bubbled into the electrolysis cell, decreasing waste in the process. Sodium carbonate is washing soda. It is used in many cleaning preparations. It is also used in the manufacture of glass, paper, soap and many other chemicals. More than five million tons of sodium carbonate are used per year.

There are other processes for producing these compounds, although the electrolytic methods are more important. Sodium hydroxide may be produced by treating a sodium carbonate solution with a slurry of slaked lime ( $\text{Ca}(\text{OH})_2$ ):

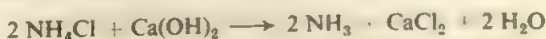


The calcium carbonate is insoluble. It precipitates, leaving the sodium hydroxide solution.

Sodium bicarbonate and sodium carbonate are produced by the *Solvay Process*. In this process, carbon dioxide and ammonia are bubbled into brine (concentrated salt solution).



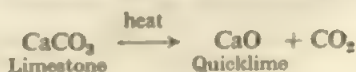
Sodium bicarbonate precipitates, due to its slight solubility in water. The crystals are collected, washed and dried. Again sodium carbonate is prepared by roasting sodium bicarbonate. The solution left behind contains ammonium chloride; it is treated with a slurry of slaked lime ( $\text{Ca}(\text{OH})_2$ ), driving off ammonia:



The ammonia is used in the original step. The  $\text{CaCl}_2$  solution is dried to gain calcium chloride, a salt used on icy roads in winter-time.

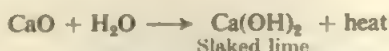
- (3) The most important *compound* of calcium is  $\text{CaCO}_3$ . Calcium carbonate occurs in vast deposits as limestone. It is used in that form as a building material. It contributes to the mortar that holds

the blocks together. Limestone is heated to  $1100^{\circ}\text{C}$  in a lime kiln to make quicklime by the elimination of carbon dioxide

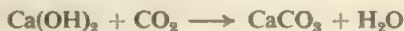


(This is the source of the carbon dioxide used in the Solvay Process and in the electrolytic production of sodium carbonate.)

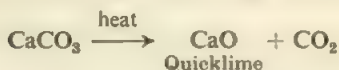
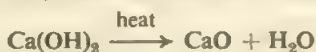
Quicklime is "slaked" by the addition of water, with a great evolution of heat:



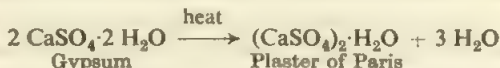
*Mortar* is made by adding 1 part calcium hydroxide and 3 parts sand with enough water to make a paste. Bricks or stone are laid with mortar between them. At first the mortar merely dries, and calcium hydroxide bonds together sand particles and bricks. In time, carbon dioxide in the air diffuses into the mortar, which is quite porous, and reacts with the hydroxide, changing it to calcium carbonate. Water escapes as vapor.



Calcium carbonate is harder than calcium hydroxide. The mortar becomes stronger with time. But heat will change either calcium carbonate or calcium hydroxide in the mortar to quicklime, which will not hold the sand particles together. Therefore a brick wall is weakened by fire and must be destroyed.



Gypsum is a hard, shiny, white, crystalline material with the formula  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . When heated, gypsum loses some of its water and becomes a white powder called "plaster of Paris."



When water is added, plaster of Paris takes up water, again forming gypsum, the hard, rocky material. Plaster of Paris cannot harden without water. This is true of portland cement, a very complicated mixture of compounds containing calcium among other elements.

## EXERCISES

1. List five general properties of metals.
2. Where are the metals found in the Periodic Table?
3. Tell what is meant by malleability, ductility and elasticity.
4. How do the properties of alloys compare with those of pure metals?



5. What kind of bonding exists between atoms in metals?
6. Why are metals better electrical conductors than are the solid non-metals?
7. What chemical property applies to all metals?
8. Why was magnesium not included among the active metals?
9. Are francium and radium active metals? Why were they not discussed?
10. Why is lithium more active with water than sodium?
11. List the alkali metals and the alkaline earth metals.
12. Write the formulas for two superoxides, two peroxides and two normal oxides.
13. Name three metals that are less dense than water.
14. Write an equation for the reaction of sodium with water.
15. Describe how sodium metal is produced.
16. State three uses for sodium metal.
17. Write equations for:
  - a. the electrolysis of molten salt.
  - b. the electrolysis of brine.
  - c. the electrolysis of brine with carbon dioxide.
18. Describe the Solvay Process.
19. Describe the preparation of mortar, starting with limestone. Describe the setting-up of mortar.
20. Why are elemental beryllium crystals much harder than the solid forms of the other elements of Group II?
21. Why should cesium have a lower melting point than sodium?
22. What two factors about a metal ion should affect the melting point of that metal?
23. How many (a) grams of sodium hydroxide, (b) liters of chlorine at STP and (c) liters of hydrogen at 10 atm and 60°C are gained by the electrolysis of 88 grams of sodium chloride in brine?
24. List all the factors that help to make the Solvay Process economically feasible?

# CHAPTER 15

## THE ACTIVE NON-METALS, THE HALOGENS

H																		H	He
Li	Be																	F	Ne
Na	Mg																	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se			Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te			I	Xe
Cs	Ba	La-	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po			At	Rn
		Lu																	
Fr	Re	Ac																	
		Lw																	

Three elements in Group VII of the Periodic Table were identified in the early part of the nineteenth century. Chlorine was prepared in 1774 by the Swedish chemist Carl Wilhelm Scheele, who is also celebrated for his discovery of oxygen two years earlier. But just as he had called oxygen "pure air" and had not appreciated the import of his discovery, he supposed chlorine to be a compound containing oxygen. Thirty-six years later Sir Humphrey Davy, finding it impossible to decompose the gas, recognized it to be an element and named it chlorine (from a Greek word meaning greenish-yellow).

Iodine was prepared in 1811 by Courtois, a manufacturer of saltpeter ( $\text{KNO}_3$ ), a component of black gunpowder. Courtois was preparing potassium from the ashes of kelp and seaweed. Treatment of the ashes with hot sulfuric acid released a dense violet vapor, which collected in glistening black crystals on a cool surface. Gay-Lussac proved that it was an element and named it after the color of its vapor. (The word iodine also derives from the Greek.)

In 1826 bromine was prepared by passing chlorine gas into the bitter

solution left when sodium chloride is crystallized from sea water. Balard, its discoverer, also named it. Its name is derived from the Greek word meaning "stench."

Although compounds of fluorine had been known for years, pure fluorine was first prepared in 1886 by Moissan. (His method will be described later in the chapter.)

Astatine (discovered in 1940), the fifth element of the group, is radioactive. It occurs in nature in a very minute amount; it is a product of the decay of actinium. The element has been prepared artificially by nuclear reactions induced by the bombardment of bismuth with alpha particles.

## 1. OCCURRENCE

These elements, known as halogens ("salt formers"), are comparatively rare, the estimated percentage in the earth's crust being: 0.1% F; 0.2% Cl; 0.001% Br; 0.001% I. However, there are readily available sources of each. Fluorine occurs in nature as fluorspar ( $\text{CaF}_2$ ) and cryolite ( $\text{Na}_3\text{AlF}_6$ ). Most naturally occurring salts of the other three elements are very soluble and have been washed or are being washed by rain and seepage into the ocean and into land-locked seas. The salts of these elements, especially sodium chloride, had been well known for centuries.

Analyses of ocean water (Atlantic Ocean) reveal about 3.5% solid residue upon evaporation. Salts of the halogens are found among other salts in this residue. Despite the small percentage of halogens and the great number of other salts, it is estimated that in one cubic mile of water there are:

128,000,000 tons NaCl  
17,900,000 tons  $\text{MgCl}_2$   
7,820,000 tons  $\text{MgSO}_4$   
4,068,000 tons  $\text{K}_2\text{SO}_4$   
350,000 tons bromine  
100 tons iodine  
45 tons silver  
9 pounds gold  
5 grams radium

Water covers approximately three-fourths of the earth's surface; there are 320,000,000 cubic miles of ocean water. This limitless source of salt was tapped by the ancients. The Romans dammed off pools of sea water and allowed the water to evaporate, leaving the salt. The important substance, so necessary for nutrition, was carried throughout the Roman Empire. Soldiers were often paid with salt (*sal*), hence the word salary. Salt is still prepared by solar evaporation.

All inland seas contain a high percentage of sodium chloride, but vary in the percentage of other salts, depending upon the soluble salts present in the area draining into the lake. The Dead Sea is 25% salt; it is especially high in magnesium chloride and iodine. Great Salt Lake, in Utah, is saturated with salts, but contains more sulfates than does ocean water. Owen's Lake, California, is relatively high in carbonates. The Stassfurt deposits

(remains of an inland sea) in Germany are high in potassium salts. Sodium chloride is also found in underground deposits, where it is either mined, or dissolved in water and pumped up as brine.

Iodine occurs in nature as an iodate. The chief compound is sodium iodate ( $\text{NaIO}_3$ ), an impurity in saltpeter ( $\text{NaNO}_3$ ), which is found in Chile.

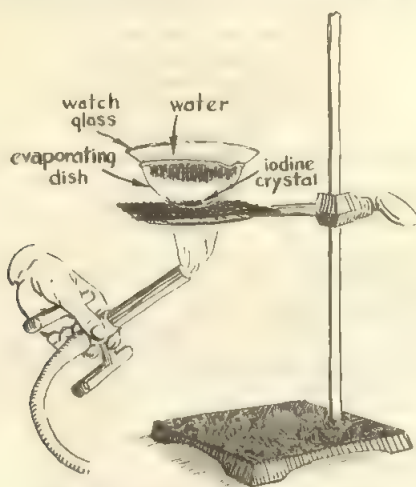
## 2. PHYSICAL PROPERTIES

Variations in the physical properties of the halogens are very much as expected from their relative positions in the Periodic Table (Table 15.1).

**Table 15.1. Properties of the Halogens**

<i>Element</i>	<i>Physical State</i>	<i>Melting Point °C</i>	<i>Boiling Point °C</i>
Fluorine, $\text{F}_2$	Light yellow gas	-223	-187
Chlorine, $\text{Cl}_2$	Greenish-yellow gas	-102	-35
Bromine, $\text{Br}_2$	Reddish-brown liquid	-7.3	+59
Iodine, $\text{I}_2$	Purple-black crystals	114	184

The color of the elements from fluorine to iodine deepens progressively (Table 15.1). As the molecular weights increase, so do the melting and



**Figure 15.1. Sublimation of iodine.**

boiling points. Whereas fluorine and chlorine are both gases at room temperature, bromine is a liquid, and iodine is a solid.

Iodine is an unusual solid in that it has a considerable vapor pressure at its melting point (90 mm at  $113.5^\circ\text{C}$ ). When heated slowly the solid is converted,



without melting, to dense violet fumes. The vapor condenses to a solid on cold surfaces in shiny black flakes, that are (except for their color) like hoarfrost. This process is called sublimation (see p. 15). It is demonstrated in the laboratory as shown in Figure 15.1. Iodine crystals heated in the evaporating dish vaporize and recrystallize on the underside of a cold watch glass which covers the dish. Iodine is purified on a commercial scale by sublimation, because the vaporizing iodine leaves non-volatile impurities as a residue.

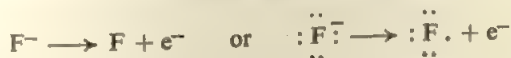
The non-polar halogens are soluble in non-polar solvents such as carbon tetrachloride and chloroform to which bromine imparts a reddish-brown color and iodine a violet color. With the exception of fluorine, which reacts violently with water, the halogens are only sparingly soluble in that solvent. Bromine is most soluble, followed by chlorine and iodine, in that order.

### 3. CHEMICAL PROPERTIES

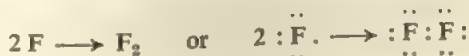
The chemical properties of the halogens are those that might be predicted by their positions in the Periodic Table. As a group they immediately precede the inert gases. With seven electrons in their valence shells they need acquire only one electron by transfer or by sharing to obtain a stable octet configuration. They are the most electronegative group of elements in the Periodic Table. The halogens and oxygen are the most active non-metals. Fluorine is the most electronegative halogen, and iodine has the least attraction (of the halogens) for valence electrons. Hence fluorine is the most reactive, with the activity decreasing successively down to iodine. The relative reactivity of the elements will be emphasized in the discussion of the preparations of the elements and their compounds. Two types of bonding are available to non-metals: ionic and covalent. The halogens take part in both. The ionic valence is  $-1$ . The  $-1$  ions, chloride, fluoride, bromide and iodide, are called halides and may be represented in equations by  $X^-$ .

### 4. PREPARATION OF THE HALOGENS

Because the halogens are never found free (uncombined) in nature, but usually occur as halides ( $\text{NaCl}$ ,  $\text{CaF}_2$ ,  $\text{MgBr}_2$ , etc.), preparation involves *oxidation* of the *halide*. Oxidation may be defined as the loss of electrons. Consider the compound fluorite ( $\text{CaF}_2$ ). It is composed of calcium ions,  $\text{Ca}^{++}$ , and fluoride ions,  $\text{F}^-$ . To prepare fluorine from fluorite, one must remove an electron from each fluoride ion:



Fluorine atoms pair to form a stable molecule:



The equation combining the two steps is:



The general *oxidation* equation for the preparation of a halogen from a halide is:



The possible methods for preparing each halogen are determined largely by the relative ease or difficulty of oxidation.

### A. PREPARATION OF FLUORINE

Fluorine has greater attraction for its valence electrons than does any other element. Likewise the fluoride ion has greater attraction for each of the eight electrons in its valence shell than does any other ion or element. For these reasons oxidation of the fluoride ion cannot be accomplished by chemicals alone. It can be done only by electrolysis; electrical energy is needed for the removal of electrons. The electrolysis cell constructed of special non-corrosive metals is very similar in operation to the Downs Cell (Fig. 14.1), which is used to prepare sodium metal and chlorine gas. Hydrogen fluoride is electrolyzed at 100°C from a liquid mixture of HF and KF. Hydrogen gas appears at the surface of the negative electrode; fluorine, at the positive electrode. To avoid explosion, the gases must be kept apart. One may check for leaks in the system by passing an unlighted cigarette or a wooden splint near the connections. Both burst into flame in a stream of fluorine.

### B. PREPARATION OF CHLORINE

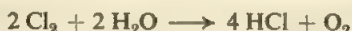
(1) Chlorine may be produced by the same method as is fluorine, that is, the electrolysis of the anhydrous, molten halide salt. (The electrolysis of sodium chloride was described in Chapter 14.)

(2) Unlike fluorine, chlorine can also be prepared in the presence of water. (Cells for the electrolysis of brine [concentrated NaCl solution] were described in Chapter 14. The products of the electrolysis are hydrogen, chlorine and a solution of sodium hydroxide.

Fluorine cannot be prepared by electrolysis of a water solution of a halide salt, because fluorine reacts rapidly with water, oxidizing and replacing the oxygen. Having lost the electrons contributed by and shared by hydrogen atoms, oxygen atoms join in pairs and escape.



Chlorine reacts with water in an analogous manner:



But the reaction is sufficiently slow to permit preparation of the gas by electrolysis of brine. (Bromine does not react with water. And not only is

iodine unreactive with water, but elemental oxygen in air will oxidize hydrogen iodide in solution to iodine, the reverse of the above reaction.



(3) Certain chemicals, *strong oxidizing agents*, have sufficient attraction for electrons to prepare chlorine from chlorides. Two of these chemicals which

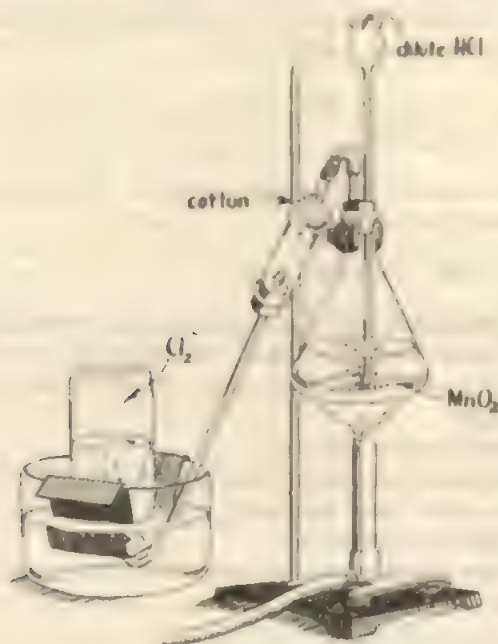
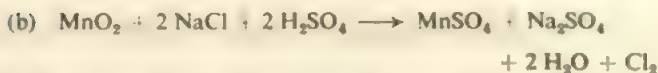
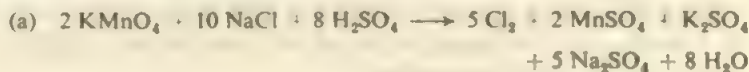


Figure 15.2. Laboratory preparation of chlorine.

will oxidize chlorides in the presence of an acid solution are potassium permanganate ( $\text{KMnO}_4$ ) and manganese dioxide ( $\text{MnO}_2$ ).



Preparation by reaction (c) is illustrated in Figure 15.2. Dilute hydrochloric acid is poured down through the thistle tube over powdered manganese dioxide. The chlorine gas is collected over water after passing through a cotton plug which removes acid droplets.

## C. PREPARATION OF BROMINE

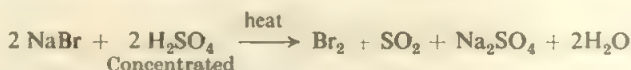
Bromine may be prepared by any method used to prepare chlorine:

(1) Electrolysis of a molten bromide salt such as sodium bromide yields bromine vapor, which is condensed to the brown liquid.

(2) Electrolysis of a bromide solution yields bromine.

(3) Strong oxidizing agents such as potassium permanganate and manganese dioxide will oxidize the bromide to bromine.

(4) Bromide may be oxidized by more mild oxidizing agents. Bromide is oxidized by hot concentrated sulfuric acid:



Bromide may be oxidized (displaced) by chlorine. The commercial preparation depends upon this reaction:

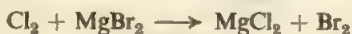


**Commercial Preparation.** The major commercial source of bromine is ocean water. As stated previously there are 350,000 tons of the bromide ion per cubic mile of water. Nevertheless, there is only 0.0008 mole of bromine per liter of solution.

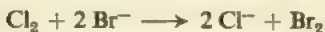
The preparation involves four steps:

(a) Crude sulfuric acid is poured into large vats of ocean water until the water is slightly acidic, about one-fourth pound acid per ton of water. This reduces the solubility of the halogens.

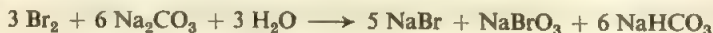
(b) Chlorine gas is bubbled into the water where it reacts with the bromide to give bromine:



or



(c) Elemental bromine has now been prepared, but in such a large amount of water that it is not colored. To concentrate the bromine into a smaller volume, air is blown through the water carrying the bromine as a vapor with it. Passage of the air through a sodium carbonate solution "strips" it of the bromine by the following reaction:



The bromine is now in a small volume as sodium bromide and sodium bromate.

(d) Acidification with sulfuric acid reverses the reaction:



restoring bromine, which is distilled from the solution.



## D. PREPARATION OF IODINE

Iodine can be prepared from the halide salt by any method used to prepare bromine.

(1) Electrolysis of a molten anhydrous iodide salt such as sodium iodide, calcium iodide or magnesium iodide yields iodine.

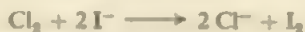
(2) Electrolysis of a concentrated iodide solution releases iodine.

(3) Strong oxidizing agents such as potassium permanganate and manganese dioxide oxidize iodide solutions.

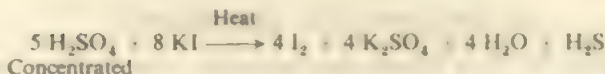
(4) Chlorine gas and hot concentrated sulfuric acid oxidize iodide to iodine as shown:



or



and



This equation represents the method used by Balard when he first discovered iodine. The seaweed ashes contained potassium iodide. Growing seaweed requires iodine, which is stored in the stems and stalks.

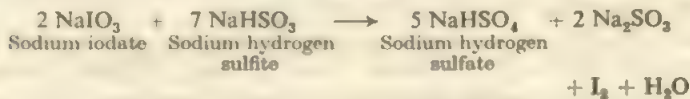
(5) Bromine oxidizes iodide solutions.



or



Iodine is sometimes obtained by oxidizing iodide found in some oil well brines and seaweed ashes. Chlorine gas is the usual oxidizing agent. However, most of the iodine used commercially is prepared from sodium iodate, an impurity in Chilean saltpeter. The iodate-containing solution left when the saltpeter is purified is treated with sodium hydrogen sulfite:

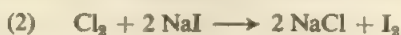
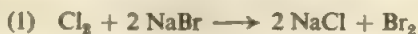


The precipitated iodine is filtered, dried and purified by sublimation.

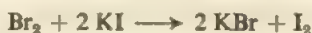
## E. GENERAL CONSIDERATIONS

The *decrease* in activity of the halogens through the series fluorine to iodine should be apparent. This explains the fact that each succeeding halogen can be prepared by all methods for the preceding one plus one or two more. The activity trend is further highlighted in that each halogen will replace in solution halide ions of any halogen that follows it. It is not practical to replace chloride or any of the other halides with fluorine, because

fluorine reacts violently with water. But chlorine replaces bromide and iodide:



and bromine replaces iodine in an iodide solution:



The reaction of chlorine with solutions of the other halides makes it useful in testing for their presence. One drop of carbon tetrachloride is added to a solution thought to contain either iodide or bromide. The  $\text{CCl}_4$  falls to the bottom. Chlorine gas is bubbled into the solution, or chlorine water is added. If the bromide ion is present, it is oxidized to bromine and dissolved in the carbon tetrachloride, which turns a reddish-brown. Any iodide present is oxidized to iodine, which dissolves in the non-polar solvent and turns it violet.

## 5. USES OF THE HALOGENS

Until recently very little fluorine was produced; now that it is available, many uses are developing. Fluorine had formerly been used to fluorinate organic compounds, but at present other, more easily controlled fluorinating reagents are used. The compounds produced may be liquids, semi-solids or plastic films and are remarkable for their chemical and thermal stability. Teflon, a plastic carbon-fluorine compound, is molded into tubing for surgical and scientific instruments. It is not attacked by acids or bases. Other fluorine-carbon compounds are used as lubricants, refrigerants, coolants, nonflammable anesthetics and insecticides, weedkillers and cleaning fluids.

Chlorine is a so-called "heavy" chemical. Large amounts, approximately two-thirds of the total production, are used for bleaching textiles and wood pulp for paper. Traces of chlorine are added to drinking water sources to kill bacteria and oxidize coloring matter. Chlorine was the first "poison gas" used in wartime, but it has been replaced by other chlorine-containing compounds, among which are phosgene and mustard gas. Chlorine is also used in the preparation of drugs, dyes and explosives.

Bromine is used to make many chemicals. Among them are tear gas, dyes and medicines. Most of the bromine is used to make ethylene dibromide ( $\text{C}_2\text{H}_4\text{Br}_2$ ), a substance added with tetraethyl lead to gasoline.

Iodine has few uses outside of the chemical laboratory. It is best known as tincture of iodine (an alcohol solution of iodine), an antiseptic used to treat wounds and abrasions of the skin. Iodine and its compounds are also used medically in treating thyroid disorders and occasionally for other diseases.

## 6. CLASSIFICATION OF HALOGEN-CONTAINING COMPOUNDS

The halogens are found in many compounds of various types. Compounds of the halogens with carbon and hydrogen in which all the bonding is covalent

are discussed in a later section of the book. The salts and acids are summarized here. It is convenient to classify these compounds by oxidation states. Table 15.2 lists some chlorine compounds. With few exceptions, there are corresponding compounds of bromine and iodine.

**Table 15.2. Oxidation States of Chlorine**

<i>Oxidation State of Chlorine</i>	<i>Acid</i>	<i>Salts</i>
-1	HCl, hydrochloric acid	KCl, potassium chloride MgCl <sub>2</sub> , magnesium chloride AgCl, silver chloride
0	Cl <sub>2</sub> , chlorine (neither acid nor salt)	
+1	HOCl, hypochlorous acid	Ca(OCl) <sub>2</sub> , calcium hypochlorite NaOCl, sodium hypochlorite
+3	HClO <sub>2</sub> , chlorous acid	NaClO <sub>2</sub> , sodium chlorite Mg(ClO <sub>2</sub> ) <sub>2</sub> , magnesium chlorite
+5	HClO <sub>3</sub> , chloric acid	KClO <sub>3</sub> , potassium chlorate Ba(ClO <sub>3</sub> ) <sub>2</sub> , barium chlorate
+7	HClO <sub>4</sub> , perchloric acid	KClO <sub>4</sub> , potassium perchlorate Ca(ClO <sub>4</sub> ) <sub>2</sub> , calcium perchlorate

There are other types of halogen-containing compounds, but most of them contain the halogen in these oxidation states. Notice that the oxidation states of the halogens extend from -1 to +7, eight units. This corresponds to the stable 8-electron configuration.

## 7. ASSIGNMENTS OF OXIDATION STATES

The oxidation state of a simple ion is its ionic valence. In potassium chloride (KCl), potassium has an oxidation state of +1, and chlorine of -1. In magnesium oxide, magnesium has an oxidation state of +2, and oxygen, -2. Table 15.3 shows the oxidation states of simple ions as they occur in some salts.

Assigning oxidation states to each element in complex ions, such as CO<sub>3</sub><sup>=</sup>, SO<sub>4</sub><sup>=</sup>, ClO<sub>3</sub><sup>=</sup> and HCO<sub>3</sub><sup>=</sup>, and in covalent compounds, such as CO<sub>2</sub>, SO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>, is more difficult and arbitrary. They are assigned as if the electrons shared by two elements were held completely by the more electronegative of the two. Hydrogen and chlorine in HCl<sub>(g)</sub> share two electrons. Chlorine, being more electronegative, is arbitrarily assigned the pair of

electrons for the assignment of oxidation states. Its oxidation state is  $-1$  whereas that of hydrogen is  $+1$ . Potassium perchlorate is an ionic compound. Therefore the potassium ion ( $K^+$ ) has an oxidation state of  $+1$ . The remaining perchlorate ion, with a charge of  $-1$ , has this configuration.



If the electrons shared by chlorine and oxygen are assigned to oxygen, the more electronegative of the two, oxygen has an oxidation state of  $-2$ , chlorine of  $+7$ .

**Table 15.3. Oxidation States of Simple Ions**

<i>Compound</i>	<i>Oxidation States of Simple Ions</i>
KCl	$K^+$ , $+1$ ; $Cl^-$ , $-1$
$MgCl_2$	$Mg^{++}$ , $+2$ ; $Cl^-$ , $-1$
NaOH	$Na^+$ , $+1$
$NaAl(SO_4)_2$	$Na^+$ , $+1$ ; $Al^{+++}$ , $+3$
$MgCO_3$	$Mg^{++}$ , $+2$
$NH_4Cl$	$Cl^-$ , $-1$
$Li_2O$	$Li^+$ , $+1$ ; $O^{=}$ , $-2$
$Na_2O_2$	$Na^+$ , $+1$

**Table 15.4. Rules for the Assignment of Oxidation States**

1. An *element* in the free state has an oxidation state of zero.
2. The oxidation state of a *simple ion* is the ionic charge.
3. Oxidation states are assigned in accordance with the rules listed below *insofar as possible* so that

- a. in *compounds* the sum of all oxidation states is zero.
- b. in *complex ions* the sum of all oxidation states is the ionic charge.

When application of two rules would violate Condition a or Condition b, the rule listed first takes precedence.

- (1) Alkali metals  $+1$
- (2) Alkaline earth metals  $+2$
- (3) Fluorine  $-1$
- (4) Hydrogen  $+1$
- (5) Oxygen  $-2$
- (6) Certain elements exhibit preferred oxidation states: Zn ( $+2$ ), Cu ( $+1$ ,  $+2$ ), Fe ( $+2$ ,  $+3$ ), Hg ( $+1$ ,  $+2$ ), Al ( $+3$ ), Cl, Br, I ( $-1$ ), etc.
- (7) Other elements are assigned such oxidation states as satisfy Conditions a and b.

Because it is tedious to assign oxidation states in this manner, and because it is difficult to remember the relative electronegativity of every element participating in covalent bonding, a simple set of rules is given in Table 15.4 for the assignment of oxidation states for each element in all compounds.



Examples for the assignment of oxidation states to all elements of a compound or complex ion are listed below:

1.  $\text{KClO}_3$ :

$$\text{K} (+1), \text{O} (-2), \text{Cl} (+5) \quad \text{for} \quad +1 + 5 + 3(-2) = 0$$

2.  $\text{Na}_2\text{O}$ :

$$\text{Na} (+1), \text{O} (-2) \quad \text{for} \quad 2(+1) - 2 = 0$$

3.  $\text{Na}_2\text{O}_2$ :

$$\text{Na} (+1), \text{O} (-1) \quad \text{for} \quad 2(+1) + 2(-1) = 0$$

4.  $\text{HClO}_2$ :

$$\text{H} (+1), \text{O} (-2), \text{Cl} (+3) \quad \text{for} \quad +1 + 3 + 2(-2) = 0$$

5.  $\text{CaH}_2$ :

$$\text{Ca} (+2) \quad \text{and} \quad \text{H} (-1) \quad \text{for} \quad +2 + 2(-1) = 0$$

6.  $\text{SO}_4^{2-}$ :

$$\text{O} (-2) \quad \text{and} \quad \text{S} (+6) \quad \text{for} \quad +6 + 4(-2) = -2$$

7.  $\text{S}_2\text{O}_3^{2-}$ :

$$\text{O} (-2) \quad \text{and} \quad \text{S} (+2) \quad \text{for} \quad 2(+2) + 3(-2) = -2$$

8.  $\text{MnO}_4^-$ :

$$\text{O} (-2) \quad \text{and} \quad \text{Mn} (+7) \quad \text{for} \quad +7 + 4(-2) = -1$$

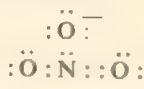
9.  $\text{CH}_2\text{O}$ :

$$\text{H} (+1), \text{O} (-2) \quad \text{and} \quad \text{C} (0) \quad \text{for} \quad 0 + 2(+1) - 2 = 0$$

10.  $\text{Fe}_3\text{O}_4$ :

$$\text{O} (-2) \quad \text{and} \quad \text{Fe} (+8/3) \quad \text{for} \quad 3 \times 8/3 + 4(-2) = 0$$

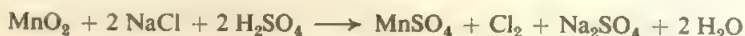
Only in the case of simple ions is the oxidation state an electrical charge. And only in the case of a simple ion is it equal to the electrons gained or lost by the atom as compared with its elemental state. At times it is merely the number of electrons contributed in sharing. In the nitrate ion, nitrogen contributes all five electrons to sharing and its oxidation state is +5. How-



ever, this relationship does not hold in all cases. The carbon in formaldehyde ( $\text{CH}_2\text{O}$ ) (oxidation state of 0) contributes four electrons to sharing. But each iron atom in  $\text{Fe}_3\text{O}_4$  does not contribute  $8/3$  electrons to sharing.

Nevertheless, oxidation states are useful. They assist in classifying compounds as in Table 15.2. They assist in identifying oxidation and reduction in equations. The change of the oxidation state of an element as it appears

in the reactants and the products shows that it has been either oxidized or reduced. If the oxidation state becomes more positive, the element is said to have been oxidized; if it becomes more negative the substance has been reduced. In these equations for the reaction of manganese dioxide, sodium chloride and sulfuric acid:



and



it can be seen that manganese has been reduced from an oxidation state of +4 to +2 while chloride ion has been oxidized from an oxidation state of -1 to 0.

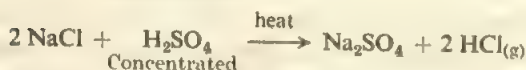
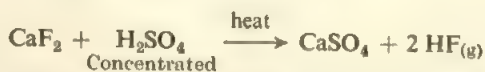
Returning to Table 15.2, one sees that the assignment of oxidation states to the halogen in the elemental form and in the series of salts and acids is in accordance with the rules. Notice the semi-systematic names. The same prefixes and suffixes are used for the corresponding bromine and iodine compounds. For example,  $\text{HBrO}$  is *hypobromous acid*;  $\text{KIO}_2$ , potassium *iodite*;  $\text{KIO}_4$ , potassium *periodate*. One should learn the suffixes and prefixes and their proper usage.

## 8. HALOGEN COMPOUNDS

### A. THE HALIDES, OXIDATION STATES OF -1

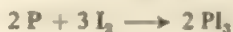
The halide salts have been discussed previously (see pp. 189-191). The importance of sodium chloride was shown in the study of the active metals: it is the commercial source of sodium metal, sodium hydroxide, sodium bicarbonate and sodium carbonate. The occurrence of sodium chloride and other halides in sea water and their use in preparing the halogens have been discussed in this chapter. The fact that table salt is essential in animal diet makes  $\text{NaCl}$  important. Of interest are the uses of sodium bromide and potassium bromide as sedatives, and the use of silver bromide in photography (to be discussed later).

The halide salts may be used with varying success to prepare the hydrogen halides. Hydrogen fluoride and hydrogen chloride are prepared commercially by heating salts with concentrated sulfuric acid.



Since they are much more volatile than hydrogen sulfate, the hydrogen halides pass off as gases. Neither  $\text{HBr}$  nor  $\text{HI}$  may be prepared by this method, because they are oxidized to the halogen by hot, concentrated sulfuric acid.

The two halides are prepared by adding water, red phosphorus and the halogen in special ways. The reactions are:

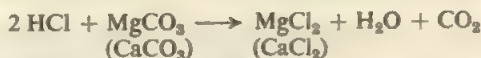


and:



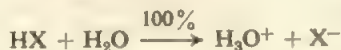
The hydrogen halides may be prepared directly from the elements. Hydrogen and fluorine will react even at  $-253^\circ\text{C}$ , at which temperature hydrogen is a liquid and fluorine a solid. When the two gases are burned together in a torch, the flame is so hot it melts rock and concrete. Hydrogen and chlorine burn smoothly together in the dark, but react explosively in sunlight. This reaction is becoming increasingly important as a commercial method of preparation. Hydrogen and bromine may be made to combine at  $200^\circ\text{C}$  in the presence of a platinum catalyst. The partial reaction of hydrogen and iodine even at a high temperature is too slow to be of importance.

Each hydrogen halide is a gas at room temperature and pressure. Each is very soluble in water. Hydrogen chloride dissolves in water up to 37 per cent or up to 12 moles of acid per liter of solution to produce concentrated hydrochloric acid. Hydrochloric acid is more important than either hydrobromic acid or hydroiodic acid simply because it is produced more cheaply. It is one of the three strong acids produced and used in the largest amounts in industry.\* Great amounts of the acid are pumped down oil wells and forced out through the porous, oil-bearing carbonate rock. It dissolves the rock, opening the pores and increasing the oil flow by this reaction:



Hydrochloric acid is used in the recovery of some metals from their ores and is used in cleaning metals. It is used in converting corn starch to dextrins, in the manufacture of soaps, glues and dyes. Hydrogen chloride is the acid found in gastric juices. The percentage varies from 0.2 to 0.4%.

Hydrofluoric acid is the only weak hydrohalic acid; that is, only a small fraction appears as ions when dissolved in water. In contrast to the other three acids, which ionize in this manner:



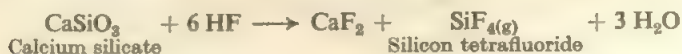
hydrofluoric acid ionizes as follows:



and does this only partially. Because hydrofluoric acid dissolves glass (which no other acid can) it is commonly thought to be the strongest acid. However, the dissolving of glass is not an acid-base reaction. Dry hydrogen fluoride

\* The other two are sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and nitric acid ( $\text{HNO}_3$ ).

dissolves glass equally as well as the acid solution. To illustrate the reaction, calcium silicate, one of the compounds in the complex silicate mixture, is used to represent glass.

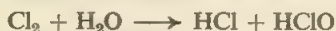


To etch designs on glass, the glass is covered with paraffin, melted in a thin film on the surface. The design is then scratched through the wax film with a sharp instrument. When the acid is placed on the glass, it dissolves the glass only where the waxy film is broken. When sufficient glass is dissolved, the hydrofluoric acid is washed away. Etching with hydrofluoric acid is important, because glass scored mechanically is weakened and breaks easily at the scratch. Etched glass retains its strength.

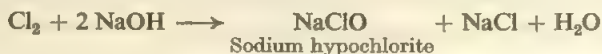
### B. SOME OXYGEN-HALOGEN COMPOUNDS

The oxyhalogen acids and salts are the most common compounds with the halogen in positive oxidation states. The halogen oxides, the oxyhalogen acids and their salts are oxidizing agents.

Chlorine gas is slightly soluble in water. It reacts slowly with water to produce hydrochloric acid and hypochlorous acid:



Chlorine gas is much more soluble in basic solutions where hypochlorites and chlorides are formed:



The hypochlorite ion attacks and oxidizes many dyes and coloring materials, making them colorless. Clorox and other bleaching solutions contain hypochlorites. The bleaching solution is made on a commercial scale by the electrolysis of brine, as described in Chapter 14, with only one change. Instead of keeping the two products—chlorine gas and sodium hydroxide solution—separate, the chlorine gas is passed through the solution. The products of the hydrolysis are sodium hypochlorite-chloride solution and hydrogen gas. Bleaching powder is made by passing chlorine gas over slaked lime.



The active hypochlorite ion is released when the salt is dissolved in water.

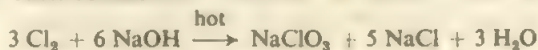
Addition of an acid such as sulfuric acid to a hypochlorite solution forms the weak acid, hypochlorous acid (HOCl). The acid is a stronger oxidizing agent than the hypochlorite ion. It is a very unstable compound and cannot be obtained in the pure state. However, the anhydride,  $\text{Cl}_2\text{O}$ , a reddish-yellow gas, may be obtained by heating a hypochlorous acid solution under partial vacuum.



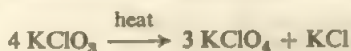
When a solution of a hypochlorite salt is heated, a chlorate salt and more chloride are formed:



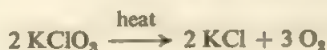
Chlorine may be converted directly to a chlorate by allowing it to dissolve in a hot basic solution:



The chlorate salts are active compounds. Potassium chlorate mixed with sulfur, sugar or charcoal is a treacherous explosive. The grinding of potassium chlorate with either of the above combustible materials may detonate the mixture. When heated carefully to the melting point ( $368^\circ\text{C}$ ), potassium chlorate decomposes slowly to potassium perchlorate and potassium chloride:



When heated to a higher temperature, oxygen is evolved:



With a catalyst the evolution of oxygen may be carried out at much lower temperatures.

Treatment of a chlorate salt with an acid is very dangerous. A reaction occurs yielding chlorine dioxide, among other products.



The reddish-yellow gas,  $\text{ClO}_2$ , is explosive, decomposing to chlorine and oxygen. Despite its explosiveness, chlorine dioxide is used extensively to bleach flour and paper. The strong and rapidly acting oxidizing agent penetrates the material to oxidize the coloring matter. The gas is prepared by reducing a chlorate solution with sulfur dioxide gas:



Acidification of a chlorate solution yields a solution of chloric acid. It is a strong acid and a good oxidizing agent. It is unstable and cannot be purified without exploding.

Perchloric acid ( $\text{HClO}_4$ ) may be prepared in solution by acidifying a solution of a perchlorate salt:



Perchloric acid is a strong oxidizing agent, but not so strong as chloric acid. However, it is more stable when heated. Nevertheless, anhydrous  $\text{HClO}_4$ , a liquid, may explode spontaneously. Being both a strong acid and a good oxidizing agent, hot concentrated perchloric acid is often used to dissolve organic matter for analysis. Solutions of more than 60% perchloric acid may explode. Therefore, water must be added, since it evaporates while the samples are being digested.

The perchlorate salts are much more stable than are the chlorate salts. They are used as oxygen sources in rocket fuels and matches in preference to the less dependable chlorates.

### EXERCISES

1. Name the four common halogens.
2. State the colors and physical states of the halogens at room temperature and pressure.
3. Why should the elemental halogens be more soluble in carbon tetrachloride than in water?
4. Explain why the color of iodine solutions in carbon tetrachloride is violet (as is iodine vapor), whereas solutions of iodine in water are brown.
5. Why is chlorine more soluble in sodium hydroxide solution than it is in water?
6. Which is the most active non-metal of all?
7. Which halogen has the greatest attraction for electrons? Why?
8. Why are fluorides not found in ocean water as are chlorides, bromides and iodides?
9. Why is it impossible to produce fluorine by the electrolysis of a solution of calcium fluoride?
10. List the steps in the preparation of bromine from sea water.
11. How can one separate iodine from non-volatile impurities?
12. Cite four sets of experimental evidence that the chemical activity of the halogens increases successively through the series iodine to fluorine.
13. List six industrial uses for the halogens.
14. Name each compound: (a)  $\text{KClO}_3$ , (b)  $\text{NaClO}_2$ , (c)  $\text{HClO}_4$ , (d)  $\text{HBrO}_3$ , (e)  $\text{HIO}_4$ , (f)  $\text{NaBrO}_2$ .
15. Determine the oxidation state of the halogen in each compound: (a)  $\text{HBrO}$ , (b)  $\text{CaCl}_2$ , (c)  $\text{NaIO}_3$ , (d)  $\text{KIO}_4$ , (e)  $\text{KBrO}_3$ , (f)  $\text{Cl}_2\text{O}$ , (g)  $\text{CHCl}_3$ , (h)  $\text{CCl}_4$ .
16. Determine the oxidation states of each element in each compound: (a)  $\text{KAl}(\text{SO}_4)_2$ , (b)  $\text{NaHCO}_3$ , (c)  $\text{CO}_2$ , (d)  $\text{Na}_2\text{O}_2$ , (e)  $\text{CH}_2\text{O}$ , (f)  $\text{Na}_3\text{AlF}_6$ , (g)  $\text{Fe}_2\text{O}_3$ , (h)  $\text{Na}_2\text{Cr}_2\text{O}_7$ , (i)  $\text{PbCrO}_4$ , (j)  $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ , (k)  $\text{NH}_4\text{Cl}$ , (l)  $\text{H}_2\text{SO}_4$ .
17. Define oxidation and reduction.
18. What acid is found in the stomach?
19. Which is the weakest acid: (a)  $\text{HF}$ , (b)  $\text{HCl}$ , (c)  $\text{HBr}$ , (d)  $\text{HI}$ ? Why?
20. What is the color of a solution of bromine in carbon tetrachloride? of potassium bromide in water?
21. Why is the heating of sodium iodide with sulfuric acid a poor way to prepare hydrogen iodide?
22. What is formed when chlorine gas is passed into a hot sodium hydroxide solution?

# CHAPTER 16

## SOLUTIONS

### 1. GENERAL ASPECTS

Solutions were discussed briefly in Chapter 4, where elements and compounds were identified and described. A solution was described as a homogeneous sample of matter that is neither element nor compound. The distinction is correct, but a positive definition is needed.

A solution is a homogeneous mixture. It is homogeneous because a sample taken from any part of it exhibits the same chemical and physical properties as any other sample. Salt water is a solution. Samples taken from various points in the liquid have the same intensity of taste, the same density, the same index of refraction and the same percentage composition.

A solution is a mixture of two or more pure substances. A compound contains two or more pure substances, but is not a mixture. Sometimes it is a very difficult laboratory problem to demonstrate that a solution is not a compound and vice versa. However, two general rules are obeyed by mixtures. (a) A mixture retains, to a large extent, the properties of the substances in the mixture. (b) A slight variation in composition causes a correspondingly slight continuous change in properties.

Contrast the product of the combination of salt and water with the product resulting from the combination of sodium and chlorine. Salt and water mix to form solutions (mixtures) of salt water. An 8% salt solution (by mass) is quite salty to the taste and has a density of 1.0559 g/ml. A 9% solution is a bit more salty and has a density of 1.0596 g/ml. Both these solutions retain the characteristic taste of salt and are very similar in appearance and density to water. Furthermore, the 9% solution is a bit more salty and a bit more dense. The density and saltiness increase steadily, with no sharp changes as more salt is added, until no more salt dissolves.

Sodium is a light (floats on water), soft, silvery metal. It burns the skin and reacts violently with water. Chlorine is a greenish-yellow, poisonous gas. When the two, sodium and chlorine, are placed together in the exact ratio of 22.990 to 35.453 parts by weight, one product, a white solid, sodium chloride, results. This compound is salty to the taste, non-corrosive and certainly non-poisonous. Sodium chloride is a typical compound, differing in properties from both of the two substances in it. A slight change in the proportions of sodium and chlorine will leave one in excess, adding its properties to those of salt.

### A. TYPES OF SOLUTIONS

There are many types of solutions. Solutions may be liquids, solids or gases. All gas mixtures are solutions. A liquid vapor in a gas is a solution. Oxygen gas is slightly soluble in water and will dissolve to form a liquid solution. Two liquids often mix to form a solution. A solid may dissolve in a liquid to form a liquid solution. Solid solutions are not well known but many occur. A gold ring is a solution of gold and copper. A silver dental filling is a solution of silver and mercury. At 300°C hydrogen gas dissolves in palladium metal to form a solid solution.

Only *binary solutions* are discussed above. A binary solution is a homogeneous mixture of *two* substances. A solution may contain many substances, but general chemistry is concerned mostly with binary solutions, binary liquid solutions, in which one of the substances is water. Most of the known chemical processes, including those of plant soil and animal chemistry, take place in water solutions.

The terms *solute* and *solvent* are often used in referring to the components of a solution. The distinction between the two is not always clear, but solvent usually refers to the substance present in greater amount or the substance that the resultant solution resembles more closely. The solute is often considered to be dissolved in the solvent. In most cases in which water is one of the substances, *it* is termed the solvent.

### B. CONCENTRATION

Because the proportion of solute to solvent may be varied, there are terms to express that proportion. In colloquial conversation, a solution is said to be "strong" or "weak." A strong solution is one containing a higher proportion of solute than usual. A weak solution has less than the usual amount of solute. Neither of these terms is precise, and each has other meanings in chemistry. In chemical language, the terms that express this ratio between solute and solvent are called concentration terms. If a solution has more than the usual amount of solute, it is said to be concentrated, or to have a high concentration. Solutions with less than the usual proportion of solute are said to be dilute, or of low concentration.

There are many quantitative terms to express concentration. The most convenient expression is usually chosen for each case. Often the term used



indicates the method of preparation. When a distinction is made between solvent and solute, the concentration is expressed in terms of the solute. Several concentration terms will be presented here, along with the method of preparation and the apparatus used.

**1. Volume Ratio.** This term is often used when both solvent and solute are liquids. It is used in cooking. A syrup containing three cups of sugar and two cups of water has a volume ratio of 3 to 2. Only volume-measuring apparatus are needed to make solutions of a definite volume ratio.

**2. Weight Per Cent and Mole Per Cent.** The concentrations of many solutions are stated in weight per cent. An 8 per cent solution has already been referred to in this chapter. An 8 per cent salt solution contains salt and water in the proportion of 8 to 92 parts by weight respectively. Of a total of 100 parts 8 parts are sodium chloride. A balance is used in making solutions of certain weight percentages. The weight of solvent and solute must be known. When the concentration is stated in per cent, it is per cent by weight, unless stated otherwise. Weights of solute and solvent are needed to calculate the mole per cent of a component of a solution. A 5 mole per cent sugar solution is one in which 5 per cent of the moles present are moles of sugar. A small quantity of a 5 mole per cent sugar solution may be made by adding 0.05 moles of sugar and 0.95 moles of water:

$$\begin{array}{rcl} 0.05 \text{ mole} \times 342 \text{ g/mole} & = & 17.10 \text{ g sugar} \\ 0.95 \text{ mole} \times 18 \text{ g/mole} & = & 17.10 \text{ g water} \\ & & \hline & & 34.20 \text{ g solution} \end{array}$$

This solution happens to be 50 per cent by weight.

An 8 per cent (by weight) salt ( $\text{NaCl}$ ) solution has a mole per cent of:

$$\frac{8 \text{ g}/58.5 \text{ g/mole}}{8 \text{ g}/58.5 \text{ g/mole} + 92 \text{ g}/18 \text{ g/mole}} \times 100 \% = 2.61 \text{ mole per cent NaCl}$$

**3. Grams per Liter and Moles per Liter, Molarity.** In chemical work the concentration of many solutions is expressed in grams of solute per liter of total solution. A solution of sodium sulfate containing 10 g/L is of such a concentration that in 1 liter of the solution there is 10 g of  $\text{Na}_2\text{SO}_4$ . Consequently, there is not exactly 1 liter of water in 1 liter of solution, but just that amount required to make the whole a liter. One uses both a balance and a volume measure to make this solution. In making one liter of the solution, 10 g of  $\text{Na}_2\text{SO}_4$  is weighed and added to a container capable of holding and measuring 1 liter (Fig. 16.1b). For precise work a volumetric flask (Fig. 16.1a) is used. Water is added with swirling to dissolve the salt; then more water is added until 1 liter of solution is prepared (Fig. 16.1b,c). This 1 liter of solution contains 10 grams. Any portion of this solution has a concentration of 10 g/L.

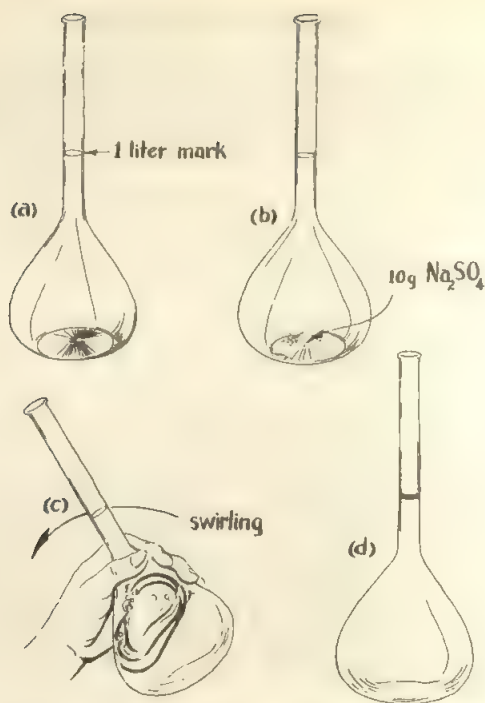


Figure 16.1. Steps in preparing a 10 g/L solution of sodium sulfate.

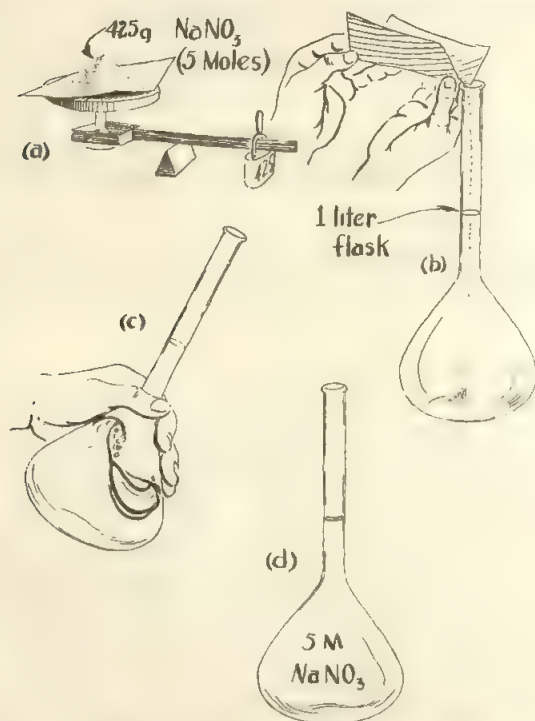


Figure 16.2. Preparation of a 5 molar solution of sodium nitrate.

The most common concentration term in analytical chemistry is *molarity*. The molarity is the concentration of a solution expressed in terms of the number of moles of solute in 1 liter of total solution. A 5 molar solution of hydrochloric acid (5 M HCl) is a solution of such a concentration that 1 liter of it contains 5 moles of dissolved hydrogen chloride.

Again, one needs equipment to measure both mass and volume to make a solution of a certain molarity. Suppose one were to make 1 liter of 5 molar sodium nitrate (5 M NaNO<sub>3</sub>). First, 5 moles of sodium nitrate:

$$5 \text{ mole} \times 85 \text{ g/mole} = 425 \text{ g}$$

are weighed on a balance (Fig. 16.2a). Second, the 425 g of NaNO<sub>3</sub> is transferred to a 1 liter flask (Fig. 16.2b). Third, water is added to dissolve the salt (Fig. 16.2c). Finally, the flask is filled to the 1 liter mark (Fig. 16.2d).

Five moles of sodium nitrate are contained in 1 liter of solution; the solution is 5 M. A solution of the same concentration can be made by dissolving 2.5 moles of NaNO<sub>3</sub> in enough water to make 500 ml of solution. Molarity does not tell "how much" solution there is, but how concentrated it is. If 1 liter of it contains 5 moles, one half liter contains 2.5 moles; one-tenth liter, 0.5 moles; but all are at the same concentration. Herein lies the value of the terminology. If 2 moles of solute is required and one has a 5 molar solution he must add 2/5 of a liter or

$$\frac{2 \text{ moles}}{5 \text{ moles/L}} \times 1000 \text{ ml/L} = 400 \text{ ml}$$

All the acids and bases used as common reagents in the laboratory are kept in an aqueous (water) solution and added in solution. The total amount of solution added is not important, but the amount (the moles) of solute is. When concentration is given in moles per liter, one can easily determine the moles added in a certain volume, as illustrated above. This concentration term will be used extensively throughout the balance of the course.

Often dilute solutions are made from more concentrated solutions by the addition of water. For example, suppose 150 ml of 1.8 M HCl solution is required and 6.0 M HCl is available. The new solution will be

$$1.8/6.0 = 0.3 \text{ as concentrated as the 6 M}$$

and therefore will contain in 10 volumes the amount of HCl contained in 3 volumes of the more concentrated solution.

$$3/10 \times 150 \text{ ml} = 45 \text{ ml}$$

$$1.8/6.0 \times 150 \text{ ml} = 45 \text{ ml}$$

Therefore, to 45 ml of 6 M HCl is added sufficient water to make 150 ml of solution.

## C. SOLUBILITY

Consider the change in density when salt is added to water at 20°C. The density increases gradually, as shown in Table 16.1 and Figure 16.3.

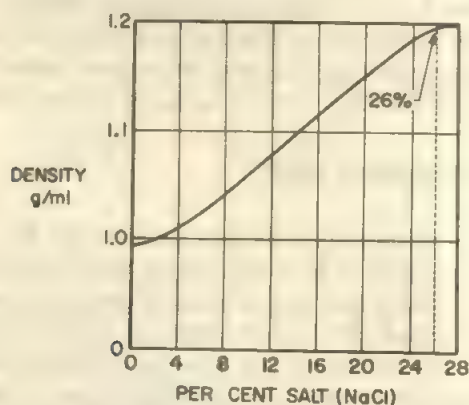


Figure 16.3. Density of salt solutions.

Table 16.1. Density of Salt Solutions

<i>Per Cent</i>	<i>Density g/ml</i>
0	0.9982
1	1.0053
4	1.0268
8	1.0559
16	1.1162
24	1.1804
26	1.1972

The gradual change in this physical property with changing composition is as expected for a solution. However, addition of more salt beyond 26% causes no change in the density of the solution. The reason is obvious to the operator, because no more salt dissolves. Neither time nor stirring can cause the salt to dissolve. The solution is said to be *saturated* with respect to salt. The concentration of the solute in the solution at saturation is its *solubility*. The concentration of table salt in the water is 26%; or in terms of molarity:

The total weight of 1 liter is:

$$1.197 \text{ g/ml} \times 1000 \text{ ml/L} = 1197 \text{ g}$$

The weight of salt in the 1 liter is:

$$1197 \text{ g/L} \times 0.26 = 311.5 \text{ g}$$



The number of moles per liter is:

$$\frac{1197 \text{ g/L} \times 0.26}{58.5 \text{ g/mole}} = 5.4 \text{ moles/liter} = 5.4 \text{ M}$$

To repeat, no more than 35 g can be dissolved in 100 g of water at 20°C. Many substances have a limited solubility in water and in other solvents as well. Some are less soluble than salt and some are more soluble, but most of

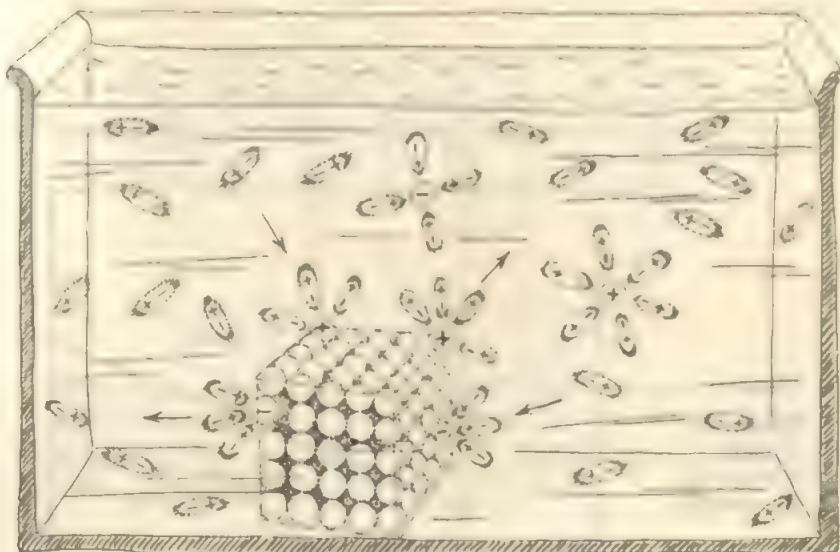


Figure 16.4. Mechanism of dissolving.

them have a limit. To see the reason for this, one must consider the mechanism of dissolving. Suppose a crystal of sodium chloride is placed in water. It begins to dissolve immediately; ions (both plus and minus) disappear from the crystal faces into the solution. Oppositely charged ions on all sides and behind in the crystal lattice hold ions of average energy securely in the crystal, but the energy of ions in a crystal follows a random distribution. Most vibrate with an energy near the average, but a few have much less energy and a few much more. The energy passes very rapidly from ion to ion by internal collisions. If an ion on the crystal surface gains sufficient energy and vibrates far enough from its position to be surrounded by polar water molecules, it may be attracted by them from the crystal. The dissolved ion is attracted by the water molecules that remain around it, so that opposite charges are together (Fig. 16.4). By this procedure ions escape into the solution continuously to become solvated by the solvent molecules. Ions never cease leaving the crystal and dissolving would appear never to stop if it were not true that ions can and do return to the crystal. When a solvated ion moving about in the solution strikes the crystal face with sufficient force, the water molecules are pushed aside. If then it rests in an exact spot left by a like ion it will remain. Despite

the "if's," this happens at a rapid and an increasing rate, as the concentration of ions in the solution increases with dissolving. Eventually the rate of ion return (crystallization) equals the rate of dissolving and the concentration of ions in the solution remains constant. A dynamic equilibrium exists at saturation.

There is experimental evidence that ions are leaving and returning to the faces of a crystal in a saturated solution. On standing, small crystals in a saturated solution grow to larger and fewer crystals without changing in amount.

#### D. TEMPERATURE EFFECT ON SOLUBILITY

Neither stirring nor powdering a solute will increase its solubility. Both aid in speedy attainment of saturation, but cannot increase the total amount that

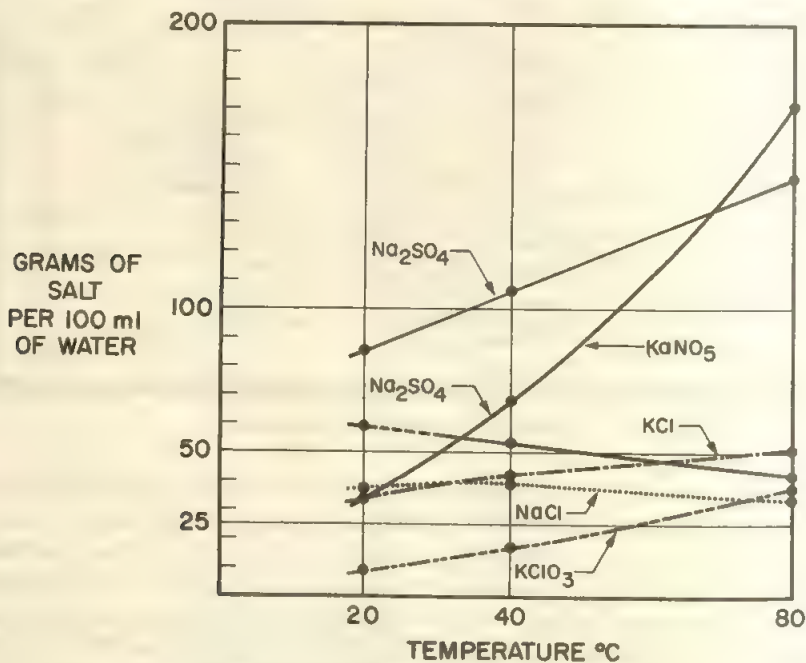


Figure 16.5. Solubilities of several salts.

dissolves. Stirring brings the crystal face in contact with a less concentrated portion of the solution and thus reduces the amount of recrystallization during dissolving. Powdering the solute increases the dissolving area, but likewise increases the recrystallization area.

A rise in temperature increases both the vibration of ions in the crystal and the movement of solvated ions in the solution and, therefore, increases both the rate of dissolving and the rate of crystallization. However, the two rates are seldom increased to the same extent. If the rate of dissolving is increased more by the increase in temperature, the solubility increases. If the rate of crystallization is increased more, the solubility is decreased.

The solubility of a group of salts in grams of solute per 100 grams of water at several temperatures is given in Table 16.2 and shown graphically in Figure 16.5.

**Table 16.2. Solubilities of Several Salts at Several Temperatures in g. 100 ml of Water and Their Respective Heats of Solution**

<i>Salt</i>	<i>Solubility at Temperature °C</i>			<i>Heat of Solution Cal/gram</i>
	20	40	80	
KCl	33	39	50	+ 60
KNO <sub>3</sub>	33	65	168	+ 84
KClO <sub>3</sub>	8	15	40	+ 83
NaCl	37	38	39	+ 22
NaNO <sub>3</sub>	88	106	147	+ 59
Na <sub>2</sub> SO <sub>4</sub>	*60	53	44	-3.88

\* metastable

In general the solubility of a salt increases with an increase in temperature, but there are notable exceptions. Five of the 6 salts listed in Table 16.2 show an increasing solubility with temperature. The solubility of table salt changes very little. The solubility of sodium sulfate decreases.

### E. HEATS OF SOLUTION

Heat effects often accompany the preparation of a solution. When 20 grams of sodium thiosulfate crystals is dissolved in 50 grams of water with stirring, the temperature of the 70 g of solution drops 10 to 12°C. In contrast, when 20 g of sodium hydroxide pellets is dissolved in 50 g of water with agitation, the temperature rises about 50°C. Heat is absorbed when sodium thiosulfate is added to water. Heat is liberated when sodium hydroxide is added to water. The heat absorbed or liberated is called the heat of solution. The heat of solution varies from solute to solute, changes with the concentration of the solution, and is proportional to the amount of solute dissolved. The molar heat of solution of sodium hydroxide in water is - 10,300 calories (exothermic); of sodium thiosulfate, +11,370 calories (endothermic).

The dissolving of most salts is endothermic. This is understandable, because ions in a crystal are held tightly by the opposite charges of adjacent ions. Each ion that escapes must gain sufficient energy to overcome the forces binding it in the lattice. As discussed previously, only the highest energy molecules are able to escape. As they escape the average energy per particle (the temperature of the crystal) decreases.

The separation of ions from a crystal is not the only process occurring when a salt dissolves. Indeed the solid would not dissolve without solvation. The

surrounding of the ion by strongly attracting polar water molecules aids in its dissolution. Just as energy is absorbed when ions are pulled from attracting particles in a lattice, energy is liberated when an ion becomes bound to a group of water molecules. The heat of solution is the difference between the binding energy of the lattice and the binding energy of the solvent molecules. If the energy required to overcome the lattice forces is greater than that regained in solution, the heat of solution is positive (endothermic). If the energy regained in solution is greater, the dissolving is exothermic.

An interesting relationship exists between the heats of solution and the change of solubility with temperature. A glance at Table 16.2 reveals that those salts whose solubility increases with temperature have a positive heat of solution, that is, the dissolving is endothermic. The one salt, sodium sulfate, whose solubility decreases with temperature, has a negative (exothermic) heat of solution. Furthermore, the greater the heat of solution, the greater the change of solubility with temperature. This relationship holds for the group of salts in Table 16.2.

#### F. SUPERSATURATION

Observe in Table 16.2 that potassium nitrate is one of the salts with an increased solubility at higher temperatures.

The solubility at:

20°C is 33 g in 100 g water

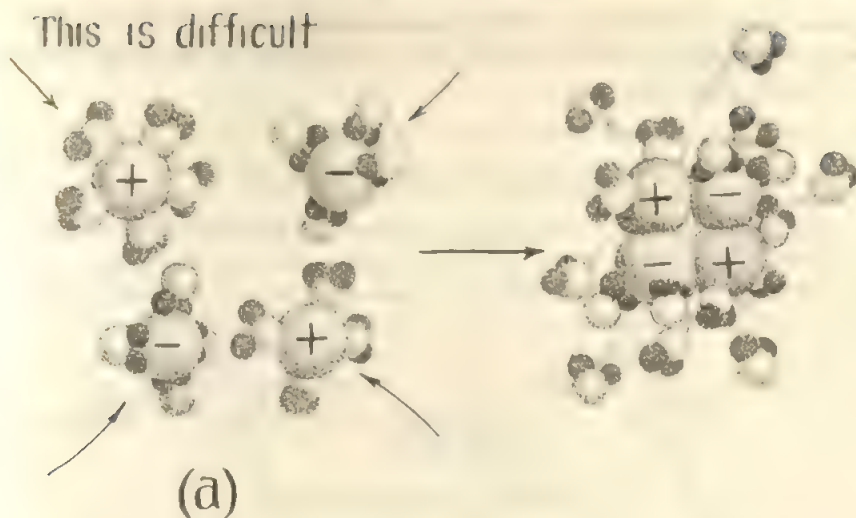
40°C is 64 g in 100 g water

80°C is 167 g in 100 g water

If 64 g of potassium nitrate is added to 100 g of water at 80°C, it will dissolve quickly and completely. Now suppose the solution is placed at room temperature and allowed to cool. One would expect that when the temperature reached and dropped just below 40°C, crystals would appear. However, this usually does not happen. If the cooling solution is kept very still, the temperature may drop to near room temperature before any crystals appear. Below 40°C, the solution is more than saturated. It is *supersaturated*. Agitation of the solution or scratching the inside of the container usually starts crystallization; adding a crystal of the solute invariably does. When crystallization does start, it proceeds rapidly, almost instantaneously, until the concentration of the solution is reduced to the solubility. The supersaturated solution becomes a saturated solution.

Saturation exists when there is a dynamic equilibrium between the solution and the solid crystals with respect to the transfer of solute ions or molecules from one to the other. In a supersaturated solution, with not one crystal of solute present, no such equilibrium is possible. It appears that the solvated ions experience difficulty in starting the first closely packed unit of the crystal (Fig. 16.6a). Once the lattice does appear, either by chance, by agitation, or





But this is relatively easy

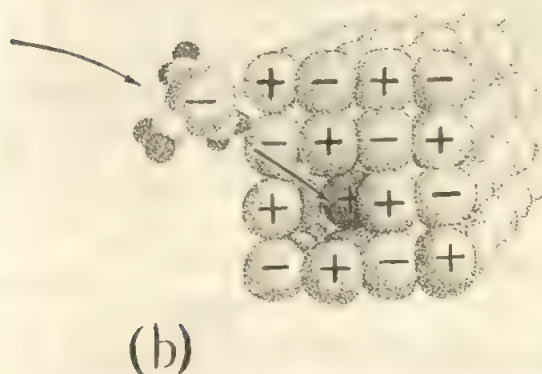


Figure 16.6. Comparison of difficulty with which ions group to start a crystal and the ease with which they can add to crystal already started.

by adding a small crystal, crystallization can and does occur. Figure 16.6b illustrates the relative ease with which ions may add to the highly attracting rigid crystal face. Equilibrium is soon attained and the solution is reduced to saturation.

## 2. COLLIGATIVE PROPERTIES OF SOLUTIONS OF NON-ELECTROLYTES

The mere presence of *any* solute in a solution modifies the physical properties of the solvent in the solution. The effects are of practical and theoretical interest. In this chapter we will consider solutions in which the solute is a

non-volatile non-electrolyte. Those properties discussed below which depend upon the number of particles of solute in a given mass of solvent are called colligative properties.

### A. LOWERING OF VAPOR PRESSURE

The vapor pressure of water above a solution is always less than the vapor pressure of pure water at the same temperature. This may be demonstrated by placing two beakers, one with water and one with a sugar solution, in a

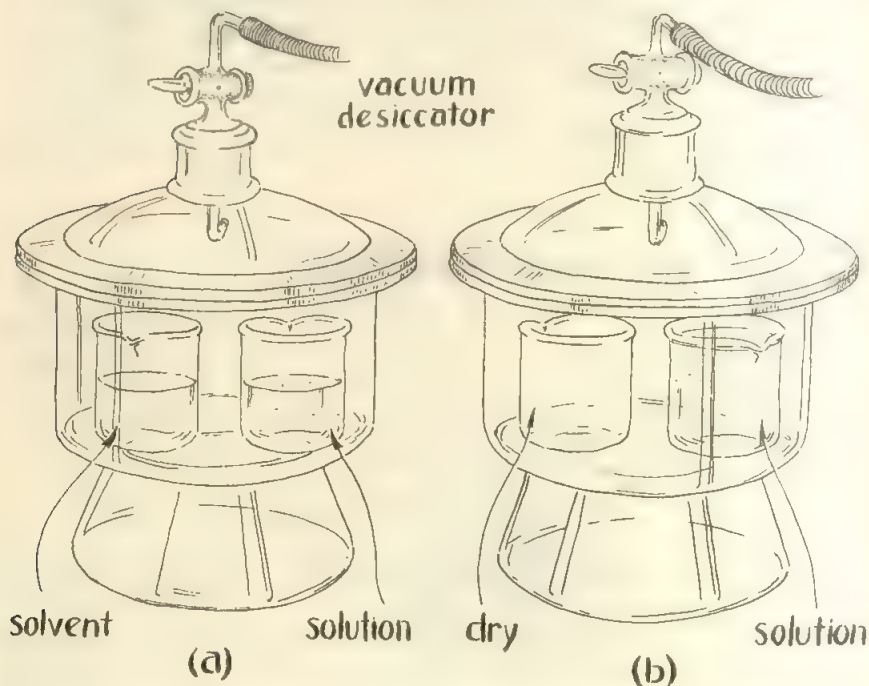


Figure 16.7. Comparison of the vapor pressure of solution and pure solvent.

vacuum desiccator (Fig. 16.7a). After they stand for a time, one can see that the volume of pure solvent has decreased, while the volume of solution has increased an equal amount. Eventually all the solvent will be transferred to the solution (Fig. 16.7b). The vapor pressure of a solution can be measured with a manometer in the same manner that one measures the vapor pressure of a pure liquid. With many solutions of non-volatile solutes, the decrease in vapor pressure is found to be proportional to the concentration of the solute.

The vapor pressure of a solution containing 1 mole of solute in 1000 g of water has a vapor pressure about  $1/55.5$  less than that of water at the same temperature. A solution containing 2 moles of sugar in 1000 g of water has a vapor pressure about  $2/55.5$  less than water.

### B. THE DECREASE IN VAPOR PRESSURE OF A SOLVENT IN A SOLUTION IS REFLECTED IN THE ELEVATION OF THE BOILING POINT

The boiling point is defined as that temperature at which the vapor pressure is 760 mm. It is obvious that, if a solution has a lower vapor pressure than the pure solvent at the same temperature, it will have a higher boiling point. A sugar solution has a lower vapor pressure at 100°C, and must be heated to a higher temperature to exert a vapor pressure of 760 mm. The increase in the boiling point by addition of a solute is proportional to the concentration of solute in the solution. A solution containing 1 mole of a non-volatile solute in 1000 g of water boils at 100.52°C. The elevation in boiling point is 0.52°C. A solution containing 1/2 mole of solute per 1000 g of water boils 0.26°C above normal or at 100.26°C.

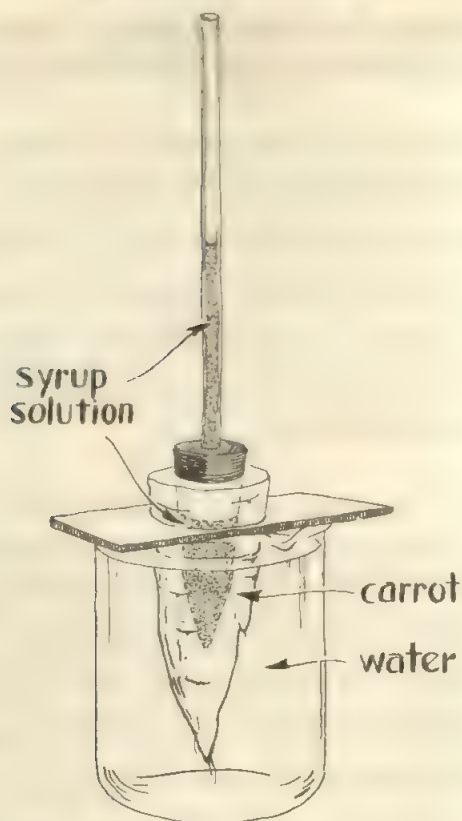
### C. DEPRESSION OF THE FREEZING POINT

It is common knowledge that ice melts when a salt is thrown upon it, even though the temperature remains below 0°C; that a mixture of milk, cream, sugar and flavoring, etc. (ice cream) will not freeze in ice water, but does freeze when surrounded by a mixture of ice, salt and water; that an addition of a solute, "antifreeze," lowers the freezing point of water as much as 60°F (33°C). All of these are examples of a depression of the freezing point of water by the addition of a solute. Again, the freezing point depression is proportional to the concentration of the solution. A solution in water of such a concentration that 1 mole of solute is contained in 1000 g of water freezes at -1.86°C; the freezing point is depressed 1.86°C. One-half mole of sugar in 1000 g of water forms a solution which freezes at -0.93°C.

### D. OSMOTIC PRESSURE

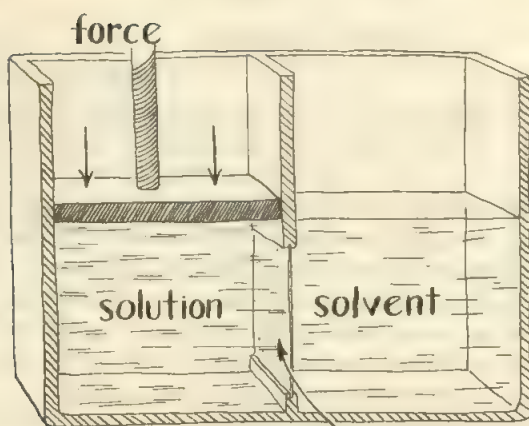
A simple experiment may be devised to observe the phenomenon, osmosis (Fig. 16.8). A carrot is hollowed out from the top and filled with a concentrated sugar syrup. A cork with a glass tubing is plugged tightly into the hole. The carrot is then placed in water. Presently the solution can be seen rising in the glass tube while the water level in the beaker falls slowly. The solution will rise several meters in the glass tube. This passage of water from the solvent through a semipermeable membrane into a solution is known as osmosis. The carrot is a semipermeable membrane. It is semi- or part permeable because water can permeate it but the solute, sugar, cannot. In osmosis, solvent passes through a semipermeable membrane from a solvent to a solution or from a solution to one of greater concentration.

Osmosis and osmotic pressure might be more easily visualized by considering the cell (Fig. 16.9). A solution of solute in water is separated from water (solvent) by a thin membrane that water alone can pass through. Osmosis occurs immediately and water flows through the membrane into the



## Osmosis

Figure 16.8. Osmosis.



semipermeable membrane

## Osmotic pressure

Figure 16.9. Osmotic pressure.



solution. This change in volumes may be arrested by forcing a piston down on the solution. At a certain force per square inch (pressure), the flow stops. If the pressure is increased, the flow of solvent is reversed. The pressure that is required above the solution to stop the osmosis is called the osmotic pressure.

Osmotic pressure has been measured as high as 250 atmospheres. The membrane in this case is a specially prepared porous cup, like a flower pot, and the solution is very concentrated because the osmotic pressure of a solution is proportional to the concentration. A solution containing 1 mole of sugar, or another non-ionizing solute, in 1000 g of water has an osmotic pressure of 24.4 atm at 25°C. A solution containing only 1/2 that amount of solute in 1000 g of water has an osmotic pressure of 12.2 atm at 25°C. Osmotic pressure increases with temperature, but it will be considered only at 25°C in this text. Plant roots gain moisture from the soil by osmosis and osmosis is also involved in the distribution of liquid in the animal body.

#### E. THE INTERRELATEDNESS OF THESE FOUR PROPERTIES IS NOT ALWAYS APPARENT

Lowering of the vapor pressure and elevation of the boiling point are, of course, directly related. Vapor pressure lowering, freezing point depression

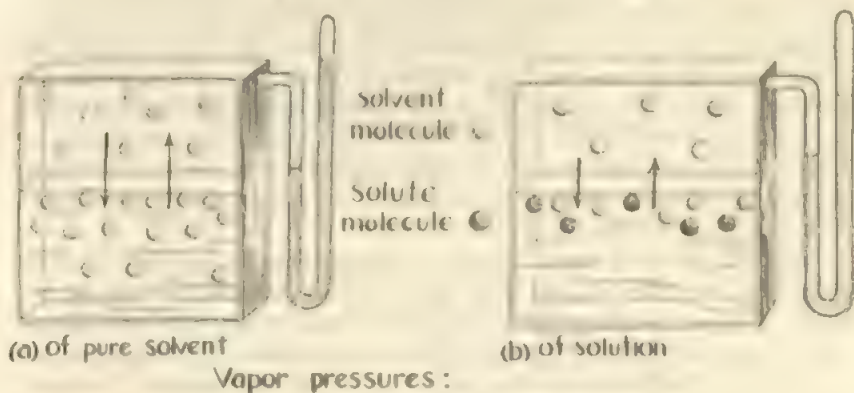


Figure 16.10. Vapor pressure.

and osmotic pressure depend on a decreased tendency for molecules of a solvent to leave the liquid when a solute is added.

The vapor pressure is lowered when a solute is added. Non-volatile solute molecules occupy positions at the surface of a solution from which solvent molecules could have escaped, thus decreasing the rate of evaporation. Correspondingly, a *smaller rate of return* is required to establish equilibrium (Fig. 16.10a,b).

The freezing point of a solvent or solution is that temperature at which there is an equilibrium between the passage of molecules from solid to liquid and

vice versa. Figure 16.11a shows the condition that exists between a solvent and its solid at the freezing point. When a solute is present, the rate of molecules leaving the solution to return to the solvent crystal is decreased (Fig. 16.11b), because fewer solvent molecules surround the crystal. To regain equilibrium, the temperature must be decreased, which, in turn, decreases the energy of vibration and decreases the number of water molecules with enough energy to leave.

Osmosis occurs and osmotic pressure exists only because molecules of solvent leave the pure solvent more rapidly than they do a solution. In

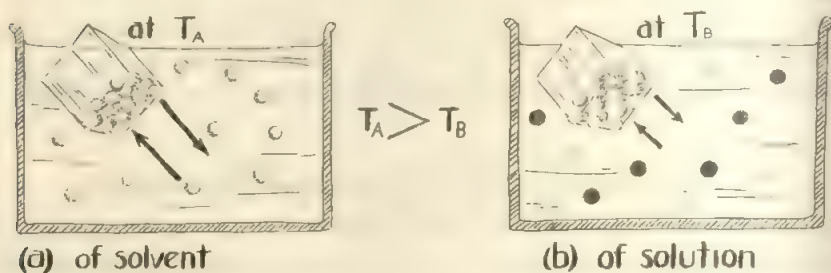


Figure 16.11. Freezing point depression.

Figure 16.12a, a semipermeable membrane separates two compartments of pure solvent. Solvent molecules move through the membrane at an equal rate in both directions and osmosis is not observed. In Figure 16.12b, the membrane separates solvent from solution. Fewer solvent molecules occupy positions against the membrane in the solution side and therefore fewer molecules pass from solution to solvent than vice versa. Osmosis results. In Figure 16.12c, sufficient pressure has been applied to the solution to increase the rate of molecules leaving the solution to the rate at which they return. This pressure is the osmotic pressure.

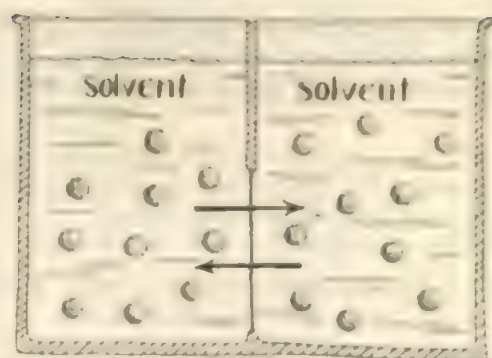
From this pictorial representation of theory, one can see that all these colligative properties should be proportional to the concentration of the solute. Further, the magnitude of the effects depend solely on the number of solute particles present. One mole of any non-volatile, non-ionizing solute should be as effective as a mole of any other in the same amount of solvent. This is the case.

#### F. CALCULATIONS

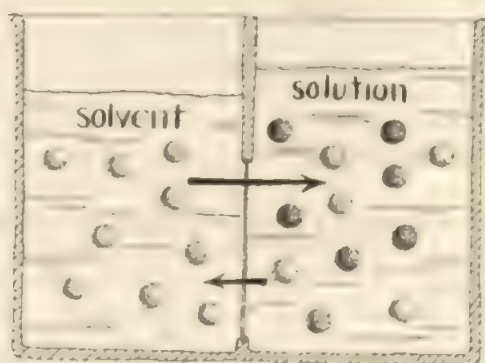
Two common calculations are associated with the colligative properties of solutions:

- (1) From the molecular weight of the solute and weight proportion of solute to solvent one can calculate the anticipated change in properties.
- (2) From the weight proportions of solute and solvent and the actual measured property one can calculate the molecular weight of the solute.

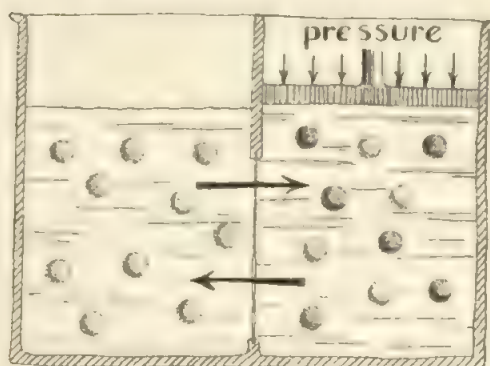
The value of each colligative property is proportional to the concentration. For example, a solute of such concentration that 1 mole of solute is contained



(a)



(b)



(c)

Figure 16.12. Osmotic pressure.

in 1000 g of water (1) will have a vapor pressure  $1/55.5$  less than that of the solvent at the same temperature, (2) will boil at  $100.52^{\circ}\text{C}$  (at 1 atm pressure), (3) will freeze at  $-1.86^{\circ}\text{C}$  and (4) has an osmotic pressure of 24.4 atm at  $25^{\circ}\text{C}$ .

**EXAMPLE 1.** Calculate the four colligative properties of a solution containing 27 g of glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) in 100 g of water.

**SOLUTION:** There are 27 g glucose per 100 g water. This corresponds to

$$\frac{27 \text{ g}}{100 \text{ g water}} \times 1000 \text{ g} = 270 \text{ g glucose per 1000 g water.}$$

This 270 g is:

$$\frac{270 \text{ g}}{180 \text{ g/mole}} = 1.5 \text{ moles of glucose}$$

a. The vapor pressure at  $25^{\circ}\text{C}$  is:

$$23.8 \text{ mm} - 1.5 \text{ mole} \times \frac{1}{55.5 \text{ mole}} \times 23.8 \text{ mm} = 23.2 \text{ mm}$$

b. The boiling point is:

$$100^{\circ}\text{C} + 0.52^{\circ}\text{C/mole} \times 1.5 \text{ mole} = 100.78^{\circ}\text{C}$$

c. The freezing point is:

$$0^{\circ}\text{C} - 1.5 \text{ mole} \times 1.86^{\circ}\text{C/mole} = -2.79^{\circ}\text{C}$$

d. The osmotic pressure at  $25^{\circ}\text{C}$  is:

$$1.5 \text{ mole} \times 24.4 \text{ atm/mole} = 36.6 \text{ atm}$$

**EXAMPLE 2.** A solution containing 6.0 g non-volatile non-electrolyte in 150 g of water freezes at  $-1.00^{\circ}\text{C}$ . Calculate the molecular weight of the solute.

**SOLUTION:** With 1000 g of water there would be:

$$6.0 \text{ g} \times \frac{1000 \text{ g}}{150 \text{ g}} = 40 \text{ g of solute}$$



But this 40 g lowers the freezing point by only 1.00 C.

$$40 \text{ g} \times \frac{1.86^\circ\text{C/mole}}{1.00^\circ\text{C}} = 74.4 \text{ g/mole}$$

would lower the freezing point to  $-1.86^\circ\text{C}$  and is therefore 1 mole.

### 3. SOLUTIONS OF LIQUIDS IN LIQUIDS

#### A. MISCIBILITY AND IMMISCIBILITY

The solubility (or insolubility) of one liquid in another is important. Alcohol and water can be dissolved together in any proportion. They are said to be completely miscible. Other pairs of liquids such as oil and water are almost totally insoluble in each other. They are said to be immiscible.

Oils and greases are soluble in carbon tetrachloride, benzene and gasoline. For this reason, these liquids have been used as dry cleaning fluids (non-water fluids). Now related liquids are often used because of the toxicity of carbon tetrachloride vapors and the flammability of the benzene and gasoline. A dry cleaning agent must be miscible with oils and must be volatile. It must be volatile so that the cleaner remaining in the fabric after cleaning evaporates readily, leaving the fabric "dry."

Laboratory experience has shown that each of these, gasoline, ether, carbon tetrachloride and benzene (Group I) are immiscible with water. Methyl alcohol, ethyl alcohol, and acetone (Group II) are all completely soluble. *The liquids within each group and often liquids from both groups are miscible.* Liquids may be classed in three groups. The liquids listed above represent Groups I and II; water, "Group III." All the liquids in Group I contain non-polar molecules. Molecules of Group II are moderately polar. Water molecules are highly polar. Non-polar liquids tend to dissolve in non-polar liquids; polar liquids, in polar liquids. Non-polar liquids and highly polar liquids are immiscible. If the attraction between like and unlike molecules is nearly the same, two liquids will mix. If attractions are very different, solubility is limited. Liquids of Group II are sufficiently polar to dissolve in water, but not too polar to be miscible with non-polar liquids.

Consider water and carbon tetrachloride. When poured together, the denser carbon tetrachloride settles in a layer at the bottom. Even after vigorous shaking, the liquids separate completely. The highly polar water molecules tend to orient themselves positive end to negative end and draw themselves tightly together, excluding the carbon tetrachloride molecules with their weak, gravity-like forces of attraction.

In summary, if the molecules of both liquids are polar, or if the molecules of both liquids are non-polar, they are likely to be miscible. However, if one liquid has polar molecules and the other non-polar molecules they are likely to be immiscible. Figure 16.13a represents polar molecules of two liquids. The molecules of the liquids attract each other and therefore

remain together. Figure 16.13b represents non-polar molecules of two liquids; there is no distinction between the attraction of the molecules and they remain together. In Figure 16.13c polar molecules are drawn together

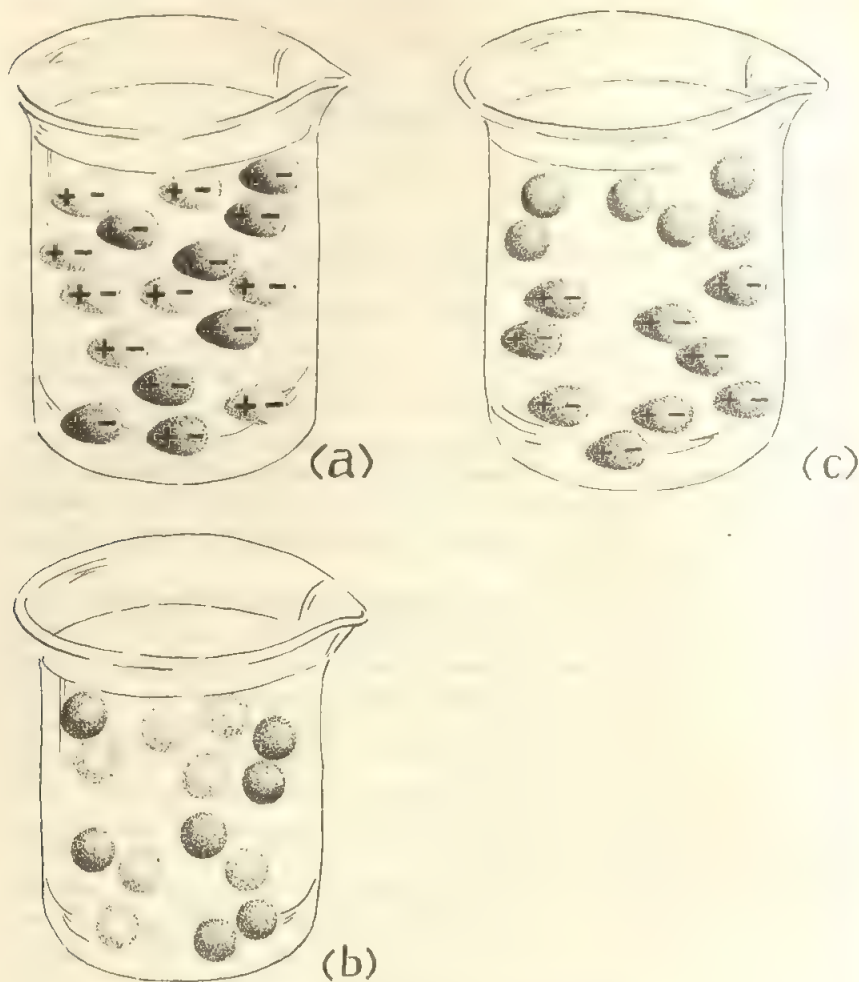


Figure 16.13. Miscibility versus polarity.

by their attraction for one another, “squeezing-out” the non-polar molecules. The two liquids remain separate, the less dense liquid forming a layer above the other.

## B. COLLIGATIVE PROPERTIES

(1) *The vapor pressure* of a solution of two liquids might be predicted if one were to consider each of them to be the solvent, with the normal lowering of vapor pressure, and then add the pressures of the two vapors together. Consider a 50 mole per cent solution of ethyl alcohol in water. Molecules in

the solution might be represented as in Figure 16.14 (even though real molecules are not lined up so neatly). One-half the molecules near the surface are water molecules. There is one-half the number of water molecules in position to escape that there would be if the liquid were pure water. It follows that the vapor pressure of water above the alcohol-water solution should be one-half that of pure water. This agrees with Raoult's Law, which states that the partial-pressure of a liquid vapor over a solution is equal to the product of the mole fraction of the liquid in the solution and the vapor pressure of the pure liquid. By the same argument, the pressure of ethyl alcohol vapor should be one-half its vapor pressure.

As a result the total vapor pressure of the solution should be intermediate between the vapor pressures of the two pure liquids. This should be reflected

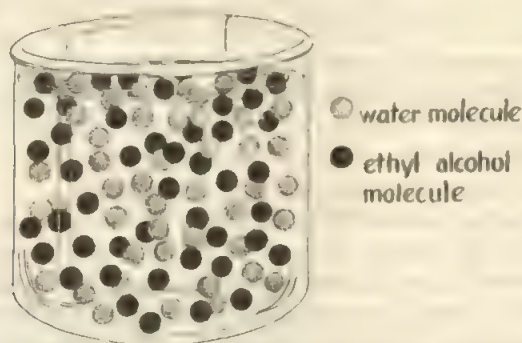


Figure 16.14. Molecules of a 50 mole per cent solution of alcohol in water.

by the boiling point of the solution, which should be intermediate between the boiling points of the two liquids. Water boils at  $100^{\circ}\text{C}$  and ethyl alcohol at  $78.5^{\circ}\text{C}$ , both at 1 atmosphere pressure. A solution containing water and alcohol in the weight ratio of 18 to 46 respectively (a 50 mole per cent solution) has a boiling point of  $79.8^{\circ}\text{C}$ . The boiling point of the solution lies between those of the two liquids, but it is nearer that of alcohol. The alcohol-water system is actually a poor example. A 95 per cent solution of alcohol in water boils at  $78.15^{\circ}\text{C}$  (somewhat below the boiling point of pure alcohol). Because less attraction exists between unlike than between like molecules, they separate more readily than expected.

It should be noted that if the alcohol has a higher vapor pressure above the 50 mole per cent water solution than does water, the vapor will contain a higher proportion of alcohol than the liquid will. While the weight per cent of alcohol in the solution is 72, 84 per cent of the vapor is alcohol. Since the vapor is more concentrated in the more volatile component than in the liquid, one might see that almost pure alcohol could be gained by vaporizing a portion of an alcohol-water solution, condensing that portion and vaporizing a portion of it, etc. This is done by fractionating columns in the alcohol industry. Repeated distillations take place up the column. Gasoline is separated from less volatile petroleum products by the same process.

Liquids have the same effect on each others' freezing points as a solid solute has. Methyl alcohol and ethylene glycol (permanent antifreeze) reduce the freezing point of water to the same extent, mole for mole, as sugar.

#### 4. SOLUTIONS OF GASES IN LIQUIDS

Solutions of gases in liquids are fully as important as liquid-liquid solutions. All marine animal life depends on oxygen dissolved in water. Fish gain oxygen for metabolism from water. Water in an aquarium must be continually replaced with fresh water, or the water must be treated. Most cold beverages contain carbon dioxide dissolved in water. Carbon dioxide bubbles from the drink when the cap is removed and imparts a crisp, sour taste.

A solution of a gas in water is prepared easily; the gas needs merely to come in contact with the liquid. The dissolving of oxygen in water can be hastened by increasing the contact of the two by spraying.

Both temperature and pressure affect the solubility of gases. Raising the temperature increases the motion of gas molecules and tends to expel them. Air can be effectively removed from water by boiling. The escaping steam carries the more active air molecules from the solution.

The amount of gas dissolved is proportional to the pressure. The greater the pressure, the greater the amount of gas that will dissolve. This is a statement of Henry's Law. Carbon dioxide is dissolved in cold drinks and the bottles capped at about five atmospheres pressure. When the pressure of carbon dioxide above the liquid is reduced to one atmosphere by removing the cap, the gas escapes by bubbling.

These rules do not apply when a chemical reaction or special chemical bonding occurs between the solvent and the gas. Hydrochloric acid and ammonia solution are both solutions of gas in water. Here bonds are formed by chemical reaction or hydration. The solubility rises to several moles per liter (about 12), compared with a small fraction for other gases (Table 16.3).

**Table 16.3. Solubility of Gases in Water in Moles per Liter of Solution at 1 atm and 0°C**

Nitrogen	$1.05 \times 10^{-3}$
Oxygen	$1.3 \times 10^{-4}$
Hydrogen	$9.6 \times 10^{-4}$
Carbon Monoxide	$1.57 \times 10^{-3}$
Hydrogen Sulfide	0.208
Ammonia	11
Hydrogen Chloride	12

#### EXERCISES

1. Define (a) homogeneous, (b) mixture, (c) solution, (d) solute, (e) solvent.
2. Distinguish between a compound and a solution on the basis of their properties and properties of their components.



3. Describe two examples of each (a) gaseous solution, (b) liquid solution, (c) solid solution.
4. What is a binary solution?
5. What is concentration?
6. Consider 3 M NaCl.
  - a. Tell what it is.
  - b. Describe steps in making 1 liter of the solution.
  - c. Describe how 500 ml of the solution is made.
7. Water is added to 200 ml of a solution of a certain molarity until the total volume is 600 ml. What is the molarity of the final solution as compared to the molarity of the original solution?
8. Define (a) saturated solution, (b) solubility, (c) dynamic equilibrium, (d) solvated molecule.
9. How does a change in temperature affect the solubility of salts? How is this effect related to the heat of solution?
10. Describe a method for preparing a supersaturated solution.
11. List four colligative properties.
12. Name at least two ways in which all four colligative properties are related.
13. Describe osmosis.
14. A solution of sugar in water has a vapor pressure 155.5 less than that of pure water at the same temperature. What is the (a) boiling point, (b) freezing point and (c) osmotic pressure of the solution at 25°C?

## PROBLEMS

1. How many moles
  - a. of oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4$ ) is 54 g?
  - b. of sodium chlorate is 100 g?
  - c. of sulfuric acid are contained in 238 g of a 20% solution?
  - d. of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  is 500 g?
2. How many moles of potassium chloride are there in 255 ml of a 6.5 M solution? How many grams?
3. How many ml of 0.75 M  $\text{Ba}(\text{NO}_3)_2$  solution may be made with 1.35 moles of  $\text{Ba}(\text{NO}_3)_2$ ? (b) with 450 g of  $\text{Ba}(\text{NO}_3)_2$ ?
4. How many grams of  $\text{H}_3\text{PO}_4$  are there in 360 ml of 3.7 M  $\text{H}_3\text{PO}_4$ ?
5. How many ml of 0.75 M  $\text{BaCl}_2$  solution must be taken to obtain 50 g of  $\text{BaCl}_2$ ?
6. Which one of these solutions contains the most  $\text{CaCl}_2$ ?
  - a. 1000 ml of 0.35 M  $\text{CaCl}_2$
  - b. 300 ml of 1.2 M  $\text{CaCl}_2$
  - c. 300 g of a 10% solution of  $\text{CaCl}_2$
7. Which solution of  $\text{H}_2\text{SO}_4$  is more concentrated, a 1 M solution or one containing 10 g per liter?
8. 200 ml of 3.4 M HCl is added to 100 ml of 1 M HCl. Calculate the concentration (in moles per liter) of the final solution.
9. Three solutions are made as follows:
  - a. 150 g NaCl is dissolved in sufficient water to make 1 L of solution.
  - b. 1 mole NaCl dissolved in sufficient water to make 300 ml of solution.
  - c. sufficient water is added to 300 ml of 3.5 M NaCl to make 400 ml of solution.
 Which solution is most dilute?
10. 35 g of HCl is added to 500 ml of 3.5 M HCl. Assume that the volume remains 500 ml. What is the final concentration?
11. What is the vapor pressure at 25°C, the osmotic pressure at 25°C, the freezing point and the boiling point for each of the solutions described below? In each case the solute is non-volatile and a non-electrolyte.
  - a. 1000 g of water + 1 mole of solute
  - b. 500 g of water + 1 mole of solute
  - c. 326 g of water + 1/2 mole of solute
  - d. 3420 g of water + 3.21 moles of solute
 The water vapor pressure table is on page 104.

12. Urea is a solid that does not ionize. Calculate the four properties requested above for the following solutions.
- 500 g of water + 60 g urea (MW = 60)
  - 100 g of water + 3.0 g urea
  - 320 g water + 7.8 g urea
13. A solution containing 500 g of water and 25 g of solute boils at  $100.52^{\circ}\text{C}$  at 1 atm.
- What is the apparent molecular weight of the solute?
  - What is the vapor pressure of the solution at  $100^{\circ}\text{C}$ ?
  - What is the freezing point of the solution?
  - What osmotic pressure will the solution exert at  $25^{\circ}\text{C}$ ?
14. What is the apparent molecular weight of the solute in each case below:
- 24 g in 360 g of water freezes at  $-1.06^{\circ}\text{C}$
  - 13.5 g in 500 g of water boils at  $100.20^{\circ}\text{C}$
  - 15 g in 750 g of water has a vapor pressure of 750 mm at  $100^{\circ}\text{C}$
  - 18.4 g in 420 g of water has an osmotic pressure of 16 atm
15. Calculate the mole per cent of alcohol in a solution made by adding 100 ml of ethyl alcohol ( $\text{C}_2\text{H}_5\text{OH}$ ) (density = 0.79 g/ml) to 100 ml of water. Answer: 23.6%
16. Calculate the freezing point of a solution containing 22.5 g of glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) in 500 g of water. Answer:  $-0.465^{\circ}\text{C}$
17. Which of these glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) solutions in water begins to freeze first when all are cooled together: (a) 50% by weight, (b) 9.1 mole per cent, (c) 2.78 M?

IONS IN SOLUTION:  
ACIDS, BASES AND SALTS

The structure of atoms has already been discussed (Chapter 6). One who understands the electrical nature of atomic structure can visualize the electrical imbalance that obtains in atoms when electrons are transferred from atom to atom in a chemical reaction. Ions (charged atoms) exist in pure substances. It might be assumed that ions exist in water solutions of the same substances.

*Arrhenius's Theory of Electrolytic Dissociation* states that this is the case. The theory may be stated in these words, "Upon addition to water certain solutes are separated into positive and negative fragments." This is an elementary concept. But one must remember that Arrhenius suggested his theory in 1887 before much was known of atomic structure, before either the electron or the proton was known. One can see in the development of this theory the determined working of the scientific method.

1. EVIDENCE FOR THE THEORY OF ELECTROLYTIC  
DISSOCIATION

The quantitative observations that led to the theory are fourfold. Each area of investigation will be discussed. Solutions of certain substances exhibited all four of the effects listed below.

## A. ABNORMAL COLLIGATIVE PROPERTIES

Some of the first experiments with colligative properties were carried out by Cavendish (the discoverer of hydrogen), who worked with the freezing point depression and found it to be proportional to the concentration of the solute. Little more was done until F. M. Raoult made an extensive series of experiments in 1881. He discovered the laws of freezing point lowering, vapor

pressure lowering and boiling point elevation that were used in the previous chapter to calculate the property changes in solution. But Raoult found numerous exceptions to his rules. While many solutes behaved as predicted, many others had a much greater effect than that calculated on the freezing and boiling points.

For example, a solution containing table salt in the ratio of 1 mole to 1000 grams of water froze at  $-3.72^{\circ}\text{C}$  and boiled at  $101.04^{\circ}\text{C}$ , the change in these properties being just double that calculated. It happened that all deviations from expected behavior were positive; a solute either changed the properties as predicted or changed them more than predicted. Many times the changes were twice, triple or quadruple the value calculated.

### B. ELECTRICAL CONDUCTIVITY

The same solutes that imparted an enhanced effect to the colligative properties of water were found to convert water into an electrical conductor.

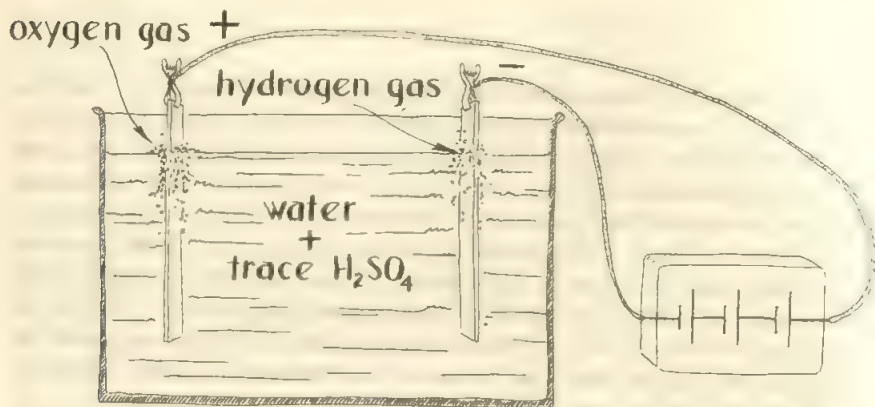


Figure 17.1. The electrolytic decomposition of water.

Electrolysis experiments had been carried out with solutions of these solutes since about 1800. At first interest centered on the fact that when wires from the two poles of a battery were placed in a solution of one of these solutes, water was decomposed and hydrogen and oxygen gases were liberated (Fig. 17.1). Later, questions arose as to the means by which the current was carried through the solution. Because their solutions carried an electric current, these solutes were called *electrolytes*. That name will be used throughout the remainder of the chapter.

### C. RAPID REACTION RATES

It was observed that reactions between electrolytes in solution occurred instantaneously. Often two electrolytes will not react together at all when pure, but when solutions of the two are added, results are immediate. This is

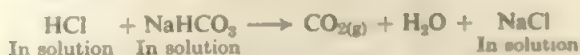


contrasted with reactions of solutions of non-electrolytes from which results may not be obtained for hours.

For example, silver nitrate crystals and sodium chloride crystals may be placed together. If they are kept perfectly dry, one can separate the crystals after an indefinite length of time with a tweezers and magnifying glass. However, when salt water is added to a silver nitrate solution, a white precipitate of silver chloride forms immediately, completely depleting one of the reactants:

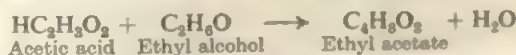


Solutions of hydrochloric acid and sodium bicarbonate react immediately to release carbon dioxide gas:



Bubbling begins and ends abruptly.

Consider the rate of reactions of solutions of two non-electrolytes, ethyl alcohol and acetic acid, to produce ethyl acetate:



Analysis of the solution formed when the two solutions are mixed reveals that several hours lapse before the maximum amount of ethyl acetate is formed.

#### D. OTHER PROPERTIES CHARACTERISTIC OF FRAGMENTS OF THE ELECTROLYTE

Solutions of the electrolytes copper sulfate, cupric chloride, copper nitrate and copper bromide are all either blue or green, the color depending somewhat on the concentration. Solutions of sodium sulfate, sodium chloride, sodium acetate, sodium oxalate and sodium nitrate are colorless, as are solutions of sodium chloride, ammonium chloride, potassium chloride and calcium chloride. In Table 17.1 these and other solutions are grouped by color or by some other distinguishing property.

**Table 17.1. Grouping of Some Electrolytes by a Common Property**

$\text{CuSO}_4$ $\text{Cu}(\text{NO}_3)_2$ $\text{CuCl}_2$ $\text{CuBr}_2$	$\left. \begin{array}{l} \text{Blue or} \\ \text{green} \end{array} \right\}$	$\text{Na}_2\text{SO}_4$ $\text{NaCl}$ $\text{NaOAc}$ $\text{Na}_2\text{C}_2\text{O}_4$	$\left. \begin{array}{l} \text{Colorless} \end{array} \right\}$	$\text{NaCl}$ $\text{NH}_4\text{Cl}$ $\text{KCl}$ $\text{CaCl}_2$	$\left. \begin{array}{l} \text{Colorless} \end{array} \right\}$
$(\text{NH}_4)_2\text{CrO}_4$ $\text{K}_2\text{CrO}_4$ $\text{Na}_2\text{CrO}_4$	$\left. \begin{array}{l} \text{Yellow} \end{array} \right\}$	$\text{HCl}$ $\text{HNO}_3$ $\text{H}_2\text{SO}_4$ $\text{H}_3\text{PO}_4$	$\left. \begin{array}{l} \text{Sour taste} \end{array} \right\}$	$\text{NaOH}$ $\text{Ca}(\text{OH})_2$ $\text{Ba}(\text{OH})_2$	$\left. \begin{array}{l} \text{Slippery feel,} \\ \text{bitter taste} \end{array} \right\}$

The table indicates that copper is blue or green in solution, sodium and chloride contribute no color, chromate is yellow, hydrogen is sour and hydroxide is slick to the touch and bitter. The properties are associated with only one part of the solute. For example, in a copper sulfate solution, the copper alone is responsible for the blue color.

The fact that solutions containing copper compounds are blue and that the blue color is contributed by copper enables the student to interpret an observation concerning conduction by solutions of electrolytes.

When a crystal of hydrated copper sulfate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) is placed in water, the blue (copper color) diffuses slowly throughout the solution. If a container of 2 or 3 liters is used, the diffusion may take hours (Fig. 17.2a).

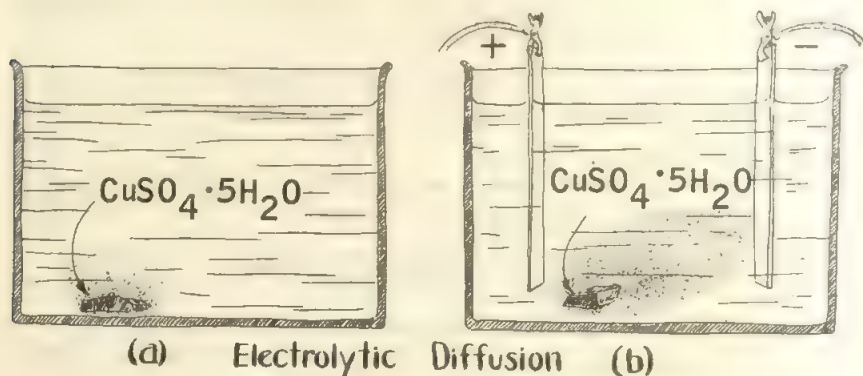


Figure 17.2. Electrolytic diffusion.

When wires from a battery cell are placed in the solution containing the crystal, the positive wire near the crystal and the negative wire on the opposite side of the container, a current flows through the circuit. While conduction occurs, the blue color of copper diffuses rapidly toward the negative electrode (Fig. 17.2b).

It should be emphasized that the electrolytes, the solutes which convert water into a conductor of electricity, are: (1) the same substances whose solutions have abnormal colligative properties, (2) the same substances which act so rapidly in solution and (3) the compounds that contribute properties to the solution characteristic of parts of their molecules. Solutions of non-electrolytes (1) do not conduct an electric current, (2) freeze at the temperature predicted, (3) may react much more slowly and (4) act as a whole unit in contributing properties to a solution.

## 2. AGREEMENT OF THEORY AND FACT

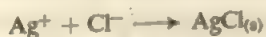
Svante Arrhenius as a college student saw a picture that explained the facts to him. This picture (theory) is embodied in the statement already quoted, "Upon addition to water, electrolytes are separated into positive and negative fragments." These fragments are now called ions.

## IMPLICATIONS OF ARRHENIUS'S THEORY

- A. If it were true, an *electric current might be carried* by the movement of the charged fragments through the solution. Positively charged ions could be drawn toward the negative electrode and negatively charged ions toward the positive electrode. The movement of the blue in copper sulfate solution toward the negative electrode might be explained if the copper fragment were the positive ion.
- B. If electrolytes are separated into positive and negative ions upon addition to water, the *colligative properties of the resulting solution would be greater* than those of a solution of a non-electrolyte of the same concentration. The colligative properties of solutions of non-electrolytes were found to depend on the concentration of molecules, regardless of their size. A solution containing 60 g of urea in 1000 g of water, and a solution containing 342 g of sugar in 1000 g of water both have the same osmotic pressure, the same freezing point, the same boiling point and the same vapor pressure. Assuming that charged particles are neither more nor less effective than molecules, one mole (58.5 g) of the simple electrolyte sodium chloride should change the colligative properties of 1000 g of water just twice as much as 342 g of sugar, because there are twice as many particles—1 mole of sodium ions and 1 mole of chloride ions.
- C. If electrolytes are separated into ions when added to water, they should *react very rapidly in solution*. Reaction between electrolytes is merely a pairing of oppositely charged ions. Consider the reaction of silver nitrate and sodium chloride in solution.



Silver and chloride fragments join and precipitate. Such ions must bear opposite charges. Assuming that the charge on the silver ion is positive, the equation becomes:



Nothing happens to the sodium and nitrate fragments. They were ions in solution before reaction and remain such afterwards. No compound is decomposed. Oppositely charged silver and chloride ions need only find one another as they move rapidly about in the solution which is very highly supersaturated with them.

- D. If an electrolyte is separated into ions when dissolved in water, *properties of the solution will be characteristic of portions of the electrolyte*. A copper nitrate solution, a copper sulfate solution, a cupric chloride solution, all contain the same copper fragment, the same copper ion,  $\text{Cu}^{++}$ , and all have the same blue color. All acid solutions contain "hydrogen ion," all are sour and all conduct electricity. The sour taste of the solution must be a property of the hydrogen fragment. If electrolytes are separated into fragments in solution, the solution should have properties of those fragments.

- E. If agreement with this fourfold evidence were insufficient to justify acceptance of the theory of electrolytic dissociation, one might consider the *reactions that occur at the electrodes in electrolytic conduction*. Brine, a solution of table salt, conducts an electric current. A cell for the electrolysis of a brine solution is diagrammed in Figure 17.3.

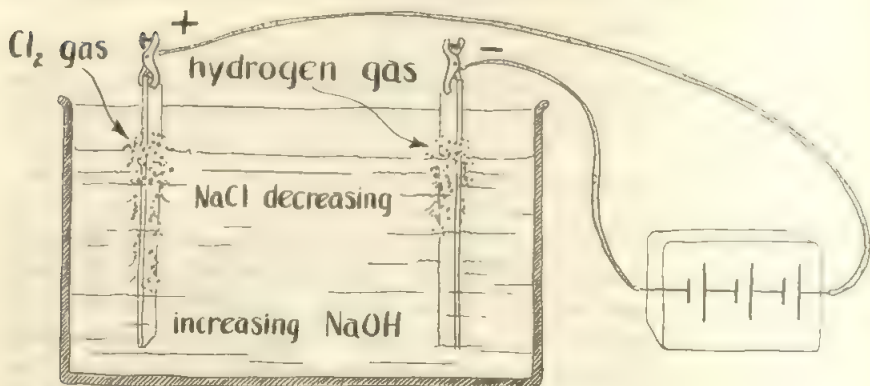


Figure 17.3. Electrolysis of brine.

Hydrogen gas bubbles form around the negative electrode. Chlorine gas bubbles up around the positive electrode, while a solution of sodium hydroxide is concentrated about the negative electrode.

Assuming that the electrolyte sodium chloride is divided into positive sodium ions and negative chloride ions dispersed among water molecules, chloride ions are drawn to the positive electrode to lose electrons to it and become neutral chlorine gas molecules.



Sodium ions are drawn to the negative electrode, where electrons are accepted by water molecules:



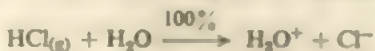
leaving hydroxide ions in solution with the sodium ions. Electrons released by chloride ions at one electrode and accepted by water molecules at the other electrode must flow through the external circuit, making an electric current. How could one explain the electrolytic process without ions?

*The ionic theory explains these phenomena discussed above and many others. In fact, as it has been amended and expanded, it is in agreement with all known evidence.*

One minor amendment of Arrhenius's Theory should be noted. Arrhenius suggested that electrolytes are "separated into ions" by the action of the water into which they are dissolved. This is true of some strong electrolytes,



namely the acids, among which is hydrochloric acid. Hydrogen chloride reacts with water according to this equation:



Neither hydronium ions nor chloride ions exist until the two molecular substances are brought together. Hydrogen chloride is *ionized literally* when dissolved. *All strong acids* exhibit covalent bonding when pure and *are ionized when dissolved in water*.

Another class of strong electrolytes are the salts, compounds that are ionic in the pure state. Table salt is one of these. Sodium ions and chloride ions are associated in an orderly arrangement in a salt crystal. When salt is dissolved in water, the ions are separated, the orderly association is broken, and salt is *dissociated*. A crystalline salt is already ionized and therefore cannot be ionized when dissolved.

### 3. WEAK ELECTROLYTES

The discussion above dealt with strong electrolytes, substances which are completely ionized in solution. Hydrogen chloride, sodium chloride and ammonium sulfate are strong electrolytes. The first two compounds have a double and the third compound a triple effect on the colligative properties of their solutions.

There are other substances that have colligative properties of a magnitude just a little greater than those of non-electrolytes and that conduct an electric current poorly. These are called weak electrolytes. They are covalent substances when pure and are not completely separated into ions by water; only a small fraction is ionized at one time. Some slightly ionized substances in solution are: acetic acid ( $\text{HC}_2\text{H}_3\text{O}_2$ ), ammonia solution ( $\text{NH}_3$ ), carbonic acid ( $\text{H}_2\text{CO}_3$ ), hydrogen sulfide ( $\text{H}_2\text{S}$ ) and many others. The most important ones will be listed later in the chapter.

### 4. TYPES OF IONIC REACTIONS

A great many reactions of electrolytes in solution are known. These reactions may be divided conveniently, though somewhat arbitrarily, into five classes.

- A. Some reactions consist merely of the "pairing" of ions to form a precipitate. The silver nitrate-sodium chloride reaction has already been cited as one of these. The reaction occurring when barium chloride solution is mixed with a solution of washing soda ( $\text{Na}_2\text{CO}_3$ ) is another example. The overall equation for the reaction is:



If dissolved, strong electrolyte substances are written as ions and the equation becomes:



All that has occurred is this:

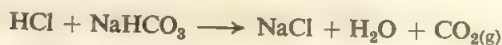


The sodium and chloride ions remain in solution.

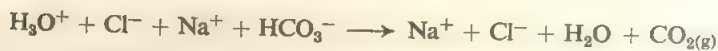
To some the equation may indicate that neutral pairs of barium and carbonate ions are formed or perhaps that neutral molecules result. This is not true. Actually, barium and carbonate ions are adding one-by-one to ionic crystals from a very supersaturated solution of the salt formed by mixing solutions containing the ions.

B. Some ions in solution combine to form a gas which escapes.

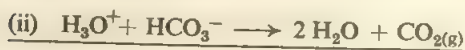
- (1) Sodium bicarbonate solution reacts with a hydrochloric acid solution to form a gas:



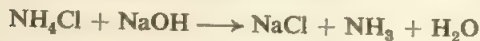
Again writing ions in solution as ions:



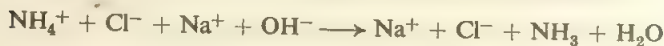
The equation becomes:



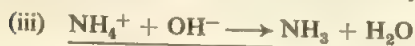
- (2) Ammonia gas may be prepared by mixing solutions of ammonium chloride and sodium hydroxide.



Writing ions in solution as ions, the equation becomes:

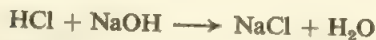


All that occurs may be represented by:

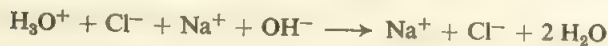


- C. Some ions in solution pair to form a *non-ionized or a weakly ionized substance or substances*.

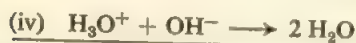
- (1) Consider the reaction of hydrochloric acid and sodium hydroxide in solution.



When ions in solution are written as ions:



the only thing that occurs is:



- (2) *Water is a very weak electrolyte, for all practical purposes a non-ionized substance.*

\* Equations marked with Roman numerals are discussed more fully later in this chapter.

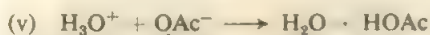
Another reaction is that of sodium acetate and hydrochloric acid.  $\text{NaC}_2\text{H}_3\text{O}_2$ , sodium acetate, may be represented by  $\text{NaOAc}$ :



In ionic form:



The process occurring is:



Slightly ionized substances, water and acetic acid, are formed.

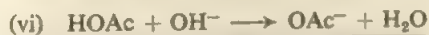
- (3) Acetic acid reacts with sodium hydroxide solution:



Again writing ions in solution as ions:



All that occurs is:

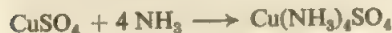


Here a slightly ionized substance,  $\text{HOAc}$ , reacts with an hydroxide ion to give the more slightly ionized substance, water.

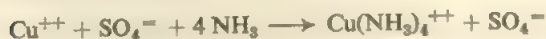
- D. In some reactions involving ions in solution, *complex ions are formed*.

- (1) When ammonia solution is added to a solution of copper sulfate, the pale blue color is changed to an intense blue. This is due to the formation of the complex ion,  $\text{Cu}(\text{NH}_3)_4^{++}$ .

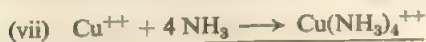
The overall equation is:



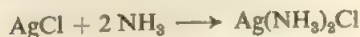
Writing ions as ions:



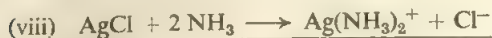
All that occurs may be represented by:



- (2) Silver chloride, a white salt insoluble in water, is dissolved by the addition of ammonia:



Writing ions in solution as ions:

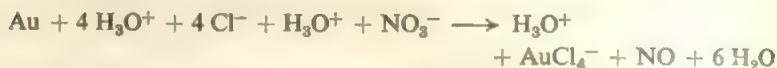


The equation represents the process which occurs on mixing.

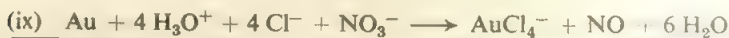
- (3) Gold will not dissolve in concentrated nitric acid, but it does dissolve in a mixture of concentrated nitric acid and concentrated hydrochloric acid by formation of a complex ion:



Writing ions as ions:



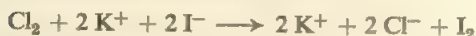
All that occurs is represented by:



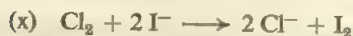
- E. Some reactions are accomplished by the *transfer of electrons* to or from or between ions.
- (1) When chlorine water is added to a solution of potassium iodide, molecular iodine is formed as evidenced by the appearance of a brown coloration. The reaction is:



Writing ions in solution as ions:



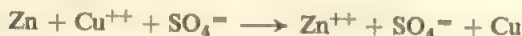
All that occurs is:



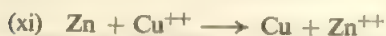
- (2) Zinc metal dissolves in a solution of copper sulfate while copper precipitates out on the zinc surface. The reaction is:



Writing free ions as ions:



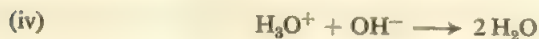
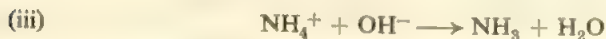
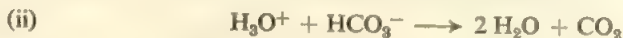
All that occurs is represented by:



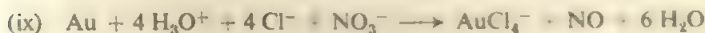
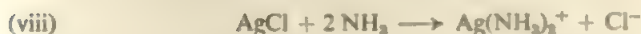
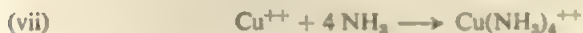
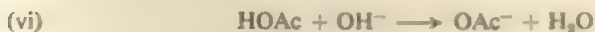
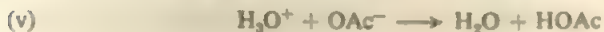
This ionic reaction is relatively slow because it depends on migration of ions to the zinc metal surface.

## 5. NET IONIC EQUATIONS

Those equations in Section 4 which were marked with small Roman numerals are called *net ionic equations*. They are reproduced below:







Each of these net ionic equations was arrived at by the same general steps: (1) The balanced overall equation was written. (2) All strong electrolytes in solution were separated into ions. Ions in solution were written as separate ions. This gives the total ionic equation. It is an attempt to show the substances in the form in which they exist at reaction time. (3) Ions which appear free and unchanged on both sides of the equation are eliminated; obviously they take no part in the reaction. They are there because the reacting ion cannot appear alone. They are often called "spectator" ions. The net ionic equation includes only the participants.

Step (2) is the only possibly difficult step of the three. One must know which ions are "ions in solution." This is a twofold problem. (a) Are they soluble (in solution) and (b) are they ions? Table 17.2 includes a statement of rules for writing net ionic equations, a list of solubilities of salts, and lists of common strong and weak electrolytes.

Both *overall* equations and net ionic equations are useful. However, each serves a different function. The *overall* equation:



may be used to calculate the reaction proportions of sodium carbonate and barium chloride. It can be used to determine the maximum possible yields of the precipitate, barium carbonate, and of the salt in solution, sodium chloride, when certain weights of reactants are used. The overall equation gives the *material balance*.

The *net ionic* equation:



states that the only thing that happens when the two water solutions of sodium carbonate and barium chloride are mixed is the precipitation of barium carbonate. In fact one could *predict this reaction* if he knew that, of the salts sodium carbonate, barium chloride, barium carbonate and sodium chloride, only barium carbonate is insoluble in water.

## Table 17.2. Net Ionic Equations

Net ionic equations show the change or changes occurring when ions in solution participate in chemical reactions. The change may be the formation or disappearance of (a) a precipitate, (b) a gas, (c) a covalent substance or a weak electrolyte, (d) a complex ion, (e) an element.

*In Net Ionic Equations*

1. Strong electrolytes in solution are written as ions.
2. Precipitates are written as molecules.
3. Covalent substances (including gases) are written as molecules.
4. Weak electrolytes are written as molecules.
5. Complex ions are written as such.
6. Ions undergoing no change are not included.

*Solubilities of Ionic Compounds*

1. All alkali metal and ammonium compounds are soluble ( $\text{KClO}_4$  is slightly soluble).
2. All nitrates are soluble.
3. All acetates are soluble ( $\text{AgC}_2\text{H}_3\text{O}_2$  is slightly soluble).
4. All sulfates are soluble, except  $\text{BaSO}_4$ ,  $\text{PbSO}_4$  and  $\text{Hg}_2\text{SO}_4$ .  $\text{CaSO}_4$  and  $\text{SrSO}_4$  are slightly soluble.
5. All chlorides, bromides and iodides are soluble, except those of  $\text{Ag}^+$ ,  $\text{Pb}^{++}$ , and  $\text{Hg}_2^{++}$ .
6. All hydroxides, phosphates, carbonates and sulfides are insoluble, except those of the alkali metals.  $\text{Ba}(\text{OH})_2$  is moderately soluble.

*Strong Electrolytes Include*

1. All ionic substances except the halides and cyanides of Hg, Cd and Zn.
2.  $\text{HClO}_4$ ,  $\text{HNO}_3$ ,  $\text{HBr}$ ,  $\text{HI}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ .

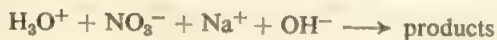
*Weak Electrolytes Include*

1.  $\text{H}_2\text{O}$ ,  $\text{HCN}$ ,  $\text{H}_2\text{CO}_3$ ,  $\text{H}_2\text{C}_2\text{O}_4$ ,  $\text{HF}$ ,  $\text{HNO}_2$ ,  $\text{HOAc}$ ,  $\text{H}_2\text{S}$ ,  $\text{HOCl}$ ,  $\text{H}_2\text{SO}_3$ ,  $\text{H}_3\text{BO}_3$ ,  $\text{H}_3\text{PO}_4$  and  $\text{NH}_3$ .

The following two examples illustrate the writing of balanced net ionic equations.

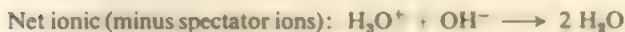
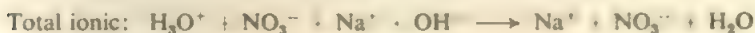
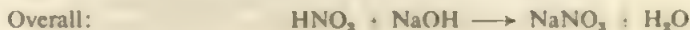
**EXAMPLE 1.** Write the net ionic equation for the reaction occurring when a solution of nitric acid ( $\text{HNO}_3$ ) is added carefully and slowly to a solution of sodium hydroxide ( $\text{NaOH}$ ).

**SOLUTION:** Table 17.2 includes  $\text{HNO}_3$  with the strong electrolytes and states that alkali metal hydroxides are soluble:



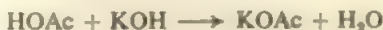
“Trading” of ions would give  $\text{NaNO}_3$ , a soluble ionic substance, and  $\text{H}_2\text{O}$ , a very weak electrolyte.

The equations are:



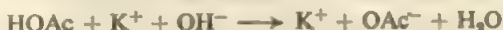
**EXAMPLE 2.** Acetic acid (HOAc) is added to a solution of potassium hydroxide. Write the net ionic equation for the reaction that occurs.

**SOLUTION:** Exchange of ions indicates that this overall equation represents the reaction:

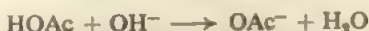


but whereas HOAc and  $\text{H}_2\text{O}$  are weakly ionized substances (weak electrolytes), KOH and KOAc are strong soluble electrolytes (Table 17.2).

The total ionic equation is:



The net ionic equation is:



## 6. ACIDS, BASES AND SALTS

### A. ACID-BASE NEUTRALIZATION

The traditional theory of acids and bases was developed throughout the nineteenth century, reaching its full stature with the publication of Arrhenius's Theory of Electrolytic Dissociation in 1887. During this period, the following criteria for acids and for bases were determined.

An acid is a substance whose solution:

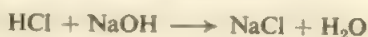
- conducts an electric current.
- has a sour taste.
- dissolves or destroys certain materials, that is, is corrosive.
- changes the color of certain naturally occurring dyes from blue to pink. (One such dye is litmus, often absorbed on paper strips and used for testing acidity.)
- reacts with solutions of bases and in so doing loses its characteristic properties.
- reacts with zinc and similar metals to produce hydrogen gas.

A base is a substance whose solution:

- conducts an electric current.
- has a bitter taste and a soapy feel.
- will dissolve or corrode certain materials.
- changes the color of certain dyes from pink to blue.
- reacts with acids, and in so doing, loses its characteristic properties.

It will be seen later that many acids and many bases do not possess all the above characteristics. Because they do not, the newer concepts of acids and bases have been formulated. Consider the following examples of acid-base reactions.

**EXAMPLE 1.** *Hydrochloric acid*, a solution of hydrogen chloride in water, agrees with all criteria for acids. A *sodium hydroxide* solution has all the characteristics of bases. Consider the reaction between the solutions, the reaction itself being one criterion:



Writing ions in solution as ions:



All that has occurred is represented by:



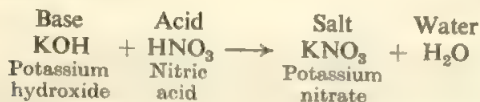
In the process, water, undissociated in solution, is formed. The resulting solution has properties of neither an acid nor a base.

Certain conclusions (not all correct) might be made from the results of this reaction:

- The so-called acid properties of a solution are properties of the hydronium ion,  $\text{H}_3\text{O}^+$ .
- Basic properties are properties of the hydroxide ion,  $\text{OH}^-$ .
- Acids and bases, or  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$ , are in a sense opposites. They are said to neutralize each other.
- Reaction of an acid and a base always produces water and an ionic compound called a salt.

These conclusions are not perfectly general, but hold for reactions of strong acids and strong bases in water solution.

**EXAMPLE 2.** The reaction of another strong acid and strong base is represented below:



Writing ions as ions:



Eliminating spectator ions:



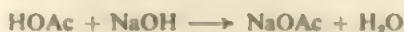
Again, all that occurs is the formation of water from the acid,  $\text{H}_3\text{O}^+$ , and the base,  $\text{OH}^-$ .

**EXAMPLE 3.** Another substance always called an acid is acetic acid,  $\text{HC}_2\text{H}_3\text{O}_2$ , (HOAc). However, an acetic acid solution does not act in



accordance with all the criteria. It is a poor conductor of electricity and will not react with zinc to produce hydrogen gas. However, the solution will react with a more reactive metal such as sodium.

Because of these limitations, acetic acid is called a weak acid. It reacts with bases:



Writing ions in solution as ions:



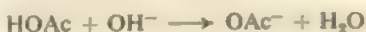
Eliminating spectator ions:



A certain small fraction of acetic acid in solution exists in ionic form, because it is a conductor, though a poor one, of electricity:



This is an equilibrium reaction. If the  $\text{H}_3\text{O}^+$  present is used up, more will be formed. However, there is no reason to believe that the  $\text{H}^+$  must be passed to a water molecule to form a  $\text{H}_3\text{O}^+$ , then passed on to the  $\text{OH}^-$  of the base. The acid properties of a solution of HOAc may not be solely those of  $\text{H}_3\text{O}^+$ . The net ionic equation:



may well portray the major course of the reaction. Again a salt solution and water are formed. The reaction of a weak acid and a base is called neutralization. This point will be discussed later.

**EXAMPLE 4.** Ammonia solution is considered a base. Again, it is a poor conductor. Ammonia solution reacts with acids:



Writing ions in solution as ions:



And the net ionic equation is:



Here the only water formed is that liberated when  $\text{H}^+$  is taken from the hydronium ion. Hydroxide ions exist in an ammonia solution:

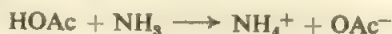


but only a very low concentration of  $\text{OH}^-$  exists. There is no reason to believe that all ammonium ions are prepared by ionization of ammonia, releasing an  $\text{OH}^-$  to form water with the hydronium ion. The formation may be direct, as shown by the net ionic equation. If so,  $\text{OH}^-$  is not the sole contributor of basic properties.

Ammonia solution and acetic acid solution can react together in neutralization:



With ions in solution written as ions:



There are no spectator ions. Ions are formed.

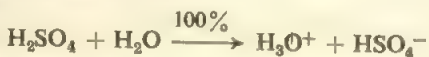
From the preceding discussion, it is apparent that any acid, strong or weak, may be neutralized by any base, strong or weak. It is obvious that *all the acids discussed above* have the same capacity to react with bases, that one mole of one of these acids in solution will neutralize the same amount of base as one mole of another. Likewise any of the bases mentioned will neutralize the same amount of acid as one mole of one of the others. Further, 1 mole of any *acid mentioned* will neutralize one mole of any *base mentioned*. This is true because each contributes either 1 mole of ( $\text{H}^+$ ) or accepts 1 mole of ( $\text{H}^+$ ).

In summary:

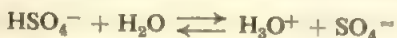
- 1 mole of HCl gives 1 mole of  $\text{H}_3\text{O}^+$  in solution ready for reaction, as does 1 mole of  $\text{HNO}_3$ .
- 1 mole of HOAc contributes 1 mole of ( $\text{H}^+$ ) for reaction with a base.
- 1 mole of KOH and 1 mole of NaOH, each furnishes 1 mole of  $\text{OH}^-$  to accept 1 mole of ( $\text{H}^+$ ).
- 1 mole of  $\text{NH}_3$  accepts 1 mole of ( $\text{H}^+$ )

## B. POLYPROTIC ACIDS AND POLYHYDROXY BASES

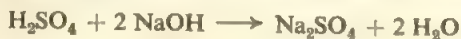
Certain other acids have a greater reacting capacity and may contribute 2 or 3 moles of hydrogen ions per mole for reaction with a base. One of these is sulfuric acid, a solution of hydrogen sulfate in water. On addition to water, hydrogen sulfate is ionized:



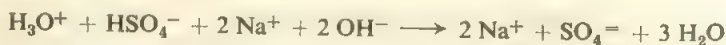
The first hydrogen is lost from all molecules to form hydronium and monohydrogen sulfate ions. Sulfuric acid is a strong electrolyte. Further ionization occurs, but only to a limited extent, because  $\text{HSO}_4^-$  is a weak acid:



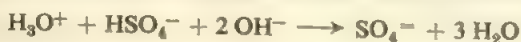
but ( $\text{H}^+$ ) may be gained from both the  $\text{H}_3\text{O}^+$  and the weak acid,  $\text{HSO}_4^-$ . One mole of  $\text{H}_2\text{SO}_4$  has twice the capacity of 1 mole of HCl in neutralization:



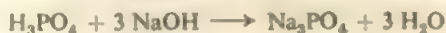
In total ionic form:



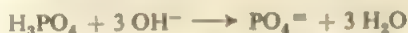
The net ionic equation represents the reaction occurring:



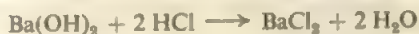
Other polyprotic acids are: sulfurous acid ( $\text{H}_2\text{SO}_3$ ); carbonic acid ( $\text{H}_2\text{CO}_3$ ); phosphoric acid ( $\text{H}_3\text{PO}_4$ ); hydrogen sulfide ( $\text{H}_2\text{S}$ ), and oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4$ ). However, these are all weak acids; only a small fraction of even the first hydrogens are transferred to water molecules and a correspondingly smaller fraction of the second hydrogens are lost. The complete neutralization of phosphoric acid is represented by these equations:



In net ionic form:



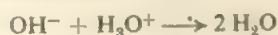
Some bases have a greater capacity than others for combining with acids. One mole of some bases may combine with 2 or 3 moles of an acid such as HCl. Barium hydroxide  $\text{Ba}(\text{OH})_2$  will accept two moles of protons per mole:



Writing ions as ions:



In net ionic form:



All strong bases release hydroxide ions when dissolved, for, like other salts, a strong base is completely ionized in the solid, and its ions are separated upon dissolving.

### C. EQUIVALENT WEIGHTS OF ACIDS AND BASES

Acids may contribute 1, 2 or 3 moles of ( $\text{H}^+$ ) per mole and bases may accept 1, 2 or 3 moles of ( $\text{H}^+$ ) per mole. Suppose weights of various acids and bases are chosen such as to be equivalent to 1 mole of hydrochloric acid in reaction capacity. To be equivalent means that it will replace or neutralize the 1 mole of HCl. Table 17.3 is a table of the *equivalent weights* of some of the common acids and bases described above.

The equivalent weight may be defined as follows: The equivalent weight is the weight of an acid or a base that will contribute or combine with 1 mole of ( $\text{H}^+$ ) in chemical reaction.

**Normality.** In reactions of acids and bases, the equivalent weight is more fundamental than the molecular weight, because 1 equivalent weight will either react with or replace any other equivalent weight. For this reason, the concentration of solutions of acids and bases are often stated in terms of the number of equivalents per liter; the *concentration in terms of equivalents per liter is the normality*. A 6 normal solution of hydrochloric acid, represented as 6 N HCl, is of such a concentration that 1 liter of the solution contains 6 equivalent weights or  $6 \times 36.5 \text{ g} = 219.0 \text{ g}$ . One-fourth liter of the same solution contains:

$$6/4 \text{ moles or } 219/4 \text{ g of HCl}$$

Consideration of a few elementary calculations may assist in understanding normalities.

**Table 17.3. Formulas, Molecular Weights and Equivalent Weights of Some Common Acids and Bases**

<i>Name</i>	<i>Formula</i>	<i>Molecular Weight</i>	<i>Equivalent Weight</i>
<b>Acids</b>			
Hydrochloric acid	HCl	36.5	36.5
Nitric acid	HNO <sub>3</sub>	63	63
Sulfuric acid	H <sub>2</sub> SO <sub>4</sub>	98	49
Acetic acid	HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	60	60
Hydrocyanic acid	HCN	27	27
Sulfurous acid	H <sub>2</sub> SO <sub>3</sub>	82	41
Phosphoric acid	H <sub>3</sub> PO <sub>4</sub>	98	32.6
Oxalic acid	H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	90	45
<b>Bases</b>			
Sodium hydroxide	NaOH	40	40
Potassium hydroxide	KOH	56	56
Barium hydroxide	Ba(OH) <sub>2</sub>	171	85.5
Calcium hydroxide	Ca(OH) <sub>2</sub>	74	37
Aluminum hydroxide	Al(OH) <sub>3</sub>	78	26
Ammonia	NH <sub>3</sub>	17	17

**EXAMPLE 1.** How many grams of H<sub>3</sub>PO<sub>4</sub> are contained in 300 ml of 2 N H<sub>3</sub>PO<sub>4</sub>?

**SOLUTION:** The equivalent weight is 1/3 the molecular weight

$$= \frac{98 \text{ g/mole}}{3 \text{ eq/mole}}$$

There are 2 equivalents/liter  
and there is:

$$\frac{300 \text{ ml}}{1000 \text{ ml/L}} = 0.3 \text{ liter}$$

$$\frac{98}{3} \text{ g/eq} \times 2 \text{ eq/L} \times \frac{300}{1000} \text{ L} = 19.6 \text{ g}$$

**EXAMPLE 2.** How many ml of 0.025 N Ca(OH)<sub>2</sub> may be made from 50 g Ca(OH)<sub>2</sub>?

**SOLUTION:** Needed for 1 liter:

$$0.025 \text{ eq/L} \times \frac{74}{2} \text{ g/eq} = 0.925 \text{ g/L}$$

There are 50 g, which is more than enough to prepare 50 liters:

$$\frac{50 \text{ g}}{0.925 \text{ g/L}} = 54.0 \text{ L.}$$



**EXAMPLE 3.** Water is added to 60 ml of 3.5 N  $\text{H}_2\text{SO}_4$  until the volume is 180 ml. What is the normality of the final solution?

**SOLUTION:** The same amount of solute is present in 180 ml as was present in 60 ml. The final solution is more dilute by the fraction 60 ml/180 ml.

$$3.5 \text{ eq/L} \times \frac{60 \text{ ml}}{180 \text{ ml}} = 1.17 \text{ eq/L} = 1.17 \text{ N}$$

Note the similarity between calculations of molarities and calculations of normalities.

#### D. TITRATIONS

Consider an experiment in which the course of a reaction between a sulfuric acid solution and a barium hydroxide solution is followed by a conductivity

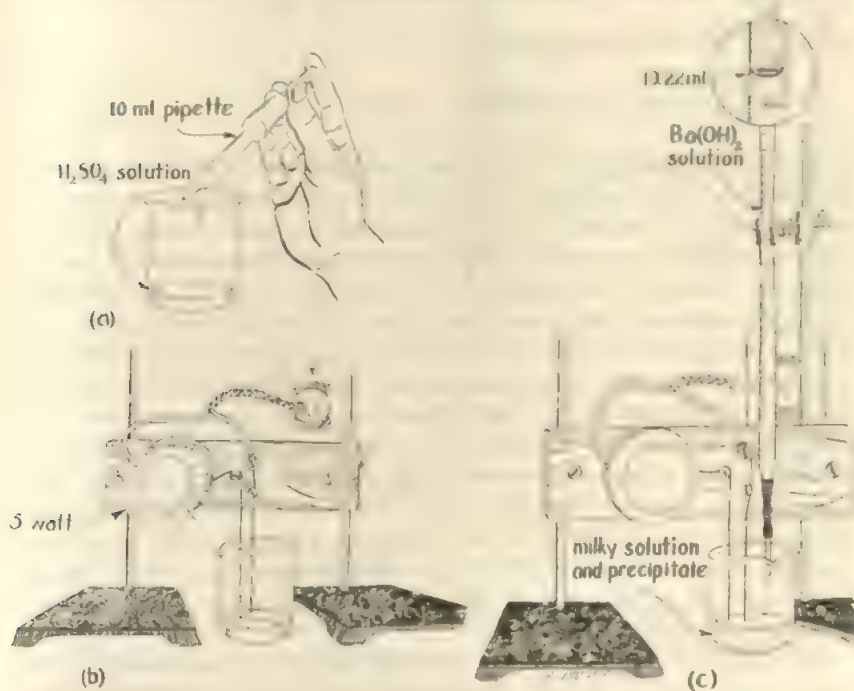


Figure 17.4. Conductometric titration.

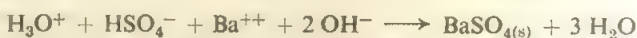
apparatus. 10 ml of a dilute sulfuric acid solution is transferred from a stock solution by a pipette to a 100 ml beaker (Fig. 17.4a). The electrodes of a conductivity apparatus are dipped into the solution and the light globe glows brightly (Fig. 17.4b). A 0.12 N  $\text{Ba(OH)}_2$  solution is added in portions from a burette with stirring (Fig. 17.4c). With the first addition of the hydroxide solution, a white precipitate appears, which becomes heavier as more base is added. Simultaneously the light dims. When 19.22 ml are added, the light is extinguished (Fig. 17.4c). Addition of one more drop of barium hydroxide

solution causes the light to glow dimly. The intensity of the light increases steadily as more base is added.

The reaction of the two solutions may be represented by these equations: Overall:



Net ionic:



At the equivalence point, that is, when an equivalent amount of base has been added to the acid, all has been converted to insoluble barium sulfate and covalent water, and practically no ions are present in solution. 19.22 ml of 0.12 N  $\text{Ba}(\text{OH})_2$  is equivalent to (accepts the protons contributed by) 10 ml of the acid solution. The acid solution contains  $\frac{19.22}{10}$  times as many equivalents per liter as the basic solution:

$$\frac{19.22}{10} \times 0.12 \text{ eq/L} = 0.23 \text{ eq/L} = 0.23 \text{ N}$$

The process described above is called a conductometric titration. Barium hydroxide solution was titrated into the sulfuric acid solution to learn the concentration of the acid. It is a conductometric titration because conductivity measurements were used to indicate the neutralization point of the two solutions. However, this method can be used only when the salt formed is insoluble, otherwise, the conductance of the solution does not drop to zero. Certain dyes called indicators are used to indicate the point of neutralization when an acid is metered into a base, or vice versa. The most commonly used indicator is phenolphthalein, an organic compound whose structure is as complex as the spelling of its name. The indicator solution is made by dissolving 1 gram of phenolphthalein in 1 liter of 90% alcohol solution. Two drops of this solution (about 0.10 ml) is sufficient to turn 200 ml of water containing one drop of 0.10 N NaOH solution a definite pink. Any other base listed previously in this chapter will turn phenolphthalein pink. On the other hand 200 ml of water, or 200 ml of any acid solution remain colorless when the indicator is added.

If a sodium hydroxide solution is added slowly to a solution of an acid containing a drop or two of phenolphthalein, no color will appear until the acid has been consumed by the reaction and one more drop of base has been added. Titrations make use of this fact.

A representative titration may be carried out in this manner. Exactly 10 ml of 0.201 M HCl is transferred from a stock solution with a pipette to a 125 ml Erlenmeyer flask (Fig. 17.5a). Two drops of indicator solution and about 50 ml of distilled water are added to give sufficient volume (Fig. 17.5b). A 50 ml burette is rinsed with distilled water and with a sodium hydroxide solution of unknown concentration, and it is finally filled with that solution to the zero mark. Readings are made at the bottom of the meniscus

(Fig. 17.5c). Sodium hydroxide solution is then added to the acid solution with swirling or mixing. Near the end point (neutralization point) the solution surrounding the drop of base just added turns pink and trails around with swirling until it disappears. When the transient color appears, the base is added dropwise, swirling after each drop until a pink color is obtained which remains for at least 30 seconds. Dissolving  $\text{CO}_2$  from the air will eventually make the solution acidic if it is let stand.

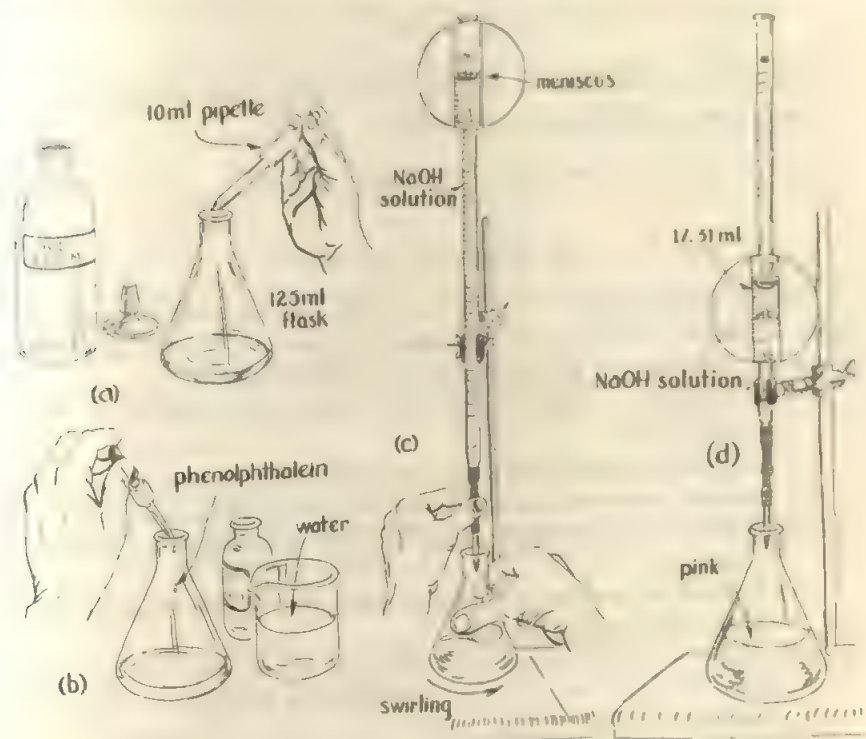


Figure 17.5. Titration.

Suppose the first permanent pink is obtained when 17.31 ml of NaOH has been added. At this point an excess of base has been added, but it is a negligible excess. One can now calculate the normality of the base.

**EXAMPLE 1.** What is the concentration of a solution of sodium hydroxide if 17.31 ml is required to neutralize 10 ml of 0.201 N HCl?

**SOLUTION:** The sodium hydroxide solution is more dilute than the acid solution; the concentration is:

$$0.201 \text{ N} \times \frac{10 \text{ ml}}{17.31 \text{ ml}} = 0.116 \text{ N}$$

Notice that one could determine the concentration of the acid solution if the concentration of the base to be added were known. With phenolphthalein

indicator, the base is added to the acid solution, because the change of colorless to pink is more easily detected than the reverse.

**EXAMPLE 2.** 7.41 ml of 0.351 N NaOH was required to neutralize 10 ml of an  $\text{H}_2\text{SO}_4$  solution. Find the molarity of the sulfuric acid.

**SOLUTION:** The sulfuric acid solution is more dilute than the base and has a normality of:

$$\frac{7.41 \text{ ml}}{10 \text{ ml}} \times 0.351 \text{ N} = 0.260 \text{ N H}_2\text{SO}_4$$

There are  $1/2$  as many moles as there are equivalents per liter of solution, because a mole of  $\text{H}_2\text{SO}_4$  is 2 equivalents.

$$0.260 \text{ eq/L} \times \frac{1}{2} \text{ mole/eq} = 0.130 \text{ mole/L} = 0.130 \text{ M}$$

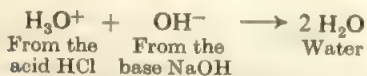
### E. ACID-BASE CONCEPTS

There are three concepts of acids and bases. Each succeeding concept is more inclusive than the preceding one. The concept is revealed by the respective definitions of acid, base, salt and neutralization.

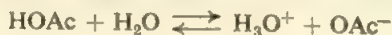
1. *The Arrhenius Concept of Acids and Bases* is the traditional idea. According to it:

- An *acid* is an electrolyte which furnishes  $\text{H}^+$  ions in solution. In more modern interpretations the hydronium ion ( $\text{H}_3\text{O}^+$ ) is furnished.
- A *base* is an electrolyte which furnishes hydroxide ions ( $\text{OH}^-$ ) in solution.
- Neutralization is the combining of the  $\text{H}_3\text{O}^+$  of the acid and the  $\text{OH}^-$  of the base to form water.
- A *salt* is an electrolyte that is neither acid nor base, that furnishes neither a  $\text{H}_3\text{O}^+$  nor an  $\text{OH}^-$ , and that may be formed, along with water, in neutralization.

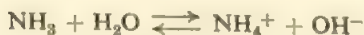
Consider the reaction of hydrochloric acid and a sodium hydroxide solution:



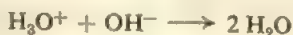
The reaction is neutralization. When the solution is evaporated, the salt, NaCl, remains. This concept includes only strong acids and bases, unless one assumes that the few  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  formed (as shown for acetic acid and ammonia):



and

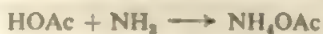


pair together:





and as they are used up more form to keep the process going. This may not be correct; much of the reaction may be direct:



2. *The Brønsted-Lowry Concept*, proposed independently by J. N. Brønsted in Denmark and T. M. Lowry in England in 1922-23, is more inclusive than the Arrhenius Theory, covering both the so-called hydrolysis reactions and reactions taking place in solutions other than water.

According to this theory:

- An *acid* is an ion or a molecule that can give up a proton ( $\text{H}^+$ ) in chemical reaction.
- A *base* is a substance or an ion of a substance that can accept a proton.
- Neutralization* is the reaction occurring when a proton ( $\text{H}^+$ ) is transferred from an acid to a base.

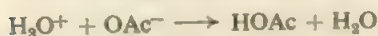
Reactions of strong acids and bases agree with this definition, because an ( $\text{H}^+$ ) is transferred from the hydronium ion to the hydroxide ion.

Consider a series of different reactions:

- Heat is evolved when hydrogen chloride gas, a covalent substance, is dissolved in water, and ions are formed. The equation for the reaction is:



- Acetic acid can be prepared by treating sodium acetate with a solution of a strong acid:



- Acetic acid will react with ammonia solution:



- Ammonia may be prepared by adding sodium hydroxide to an ammonium chloride solution.



Notice that reactions (i) to (iv) are all neutralization reactions in the Brønsted sense. In each reaction, a proton is transferred. Select the acid, the proton donor, in each equation.

Acids

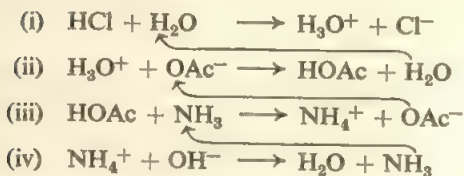
- $\text{HCl} + \text{H}_2\text{O} \longrightarrow \text{H}_3\text{O}^+ + \text{Cl}^-$
- $\text{H}_3\text{O}^+ + \text{OAc}^- \longrightarrow \text{HOAc} + \text{H}_2\text{O}$
- $\text{HOAc} + \text{NH}_3 \longrightarrow \text{NH}_4^+ + \text{OAc}^-$
- $\text{NH}_4^+ + \text{OH}^- \longrightarrow \text{H}_2\text{O} + \text{NH}_3$

Note that the acid in each succeeding equation is a product of the equation above. It is the product that results when the base accepts the proton. Obviously the acid strength decreases from the very strong acid

$\text{HCl}_{(g)}$  through the series  $\text{H}_3\text{O}^+$ ,  $\text{HOAc}$  and  $\text{NH}_4^+$  to  $\text{H}_2\text{O}$ .  $\text{HCl}_{(g)}$  will react with all the bases listed;  $\text{H}_3\text{O}^+$ , with those of (ii), (iii) and (iv);  $\text{HOAc}$ , with the bases in (iii) and (iv); while  $\text{NH}_4^+$  reacts with only  $\text{OH}^-$ .  $\text{H}_2\text{O}$  will lose a proton to none of these bases.

Now select the base, the substance that accepts the proton:

Bases



The base in each equation is a product of the succeeding equation. When the bases are listed as below, the basic strength decreases through the series:

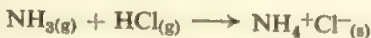


When the acids are listed in decreasing strength and the bases in increasing strength, an interesting relationship is found.

	Acids	Bases	
Strongest	HCl	$\text{Cl}^-$	Weakest
	$\text{H}_3\text{O}^+$	$\text{H}_2\text{O}$	
	HOAc	$\text{OAc}^-$	
	$\text{NH}_4^+$	$\text{NH}_3$	
Weakest	$\text{H}_2\text{O}$	$\text{OH}^-$	Strongest

In Brønsted terminology,  $\text{Cl}^-$  is the *conjugate base* of the acid  $\text{HCl}$  and  $\text{HCl}$  is the conjugate acid of the base  $\text{Cl}^-$ . Because  $\text{HCl}$  is a strong acid, loses ( $\text{H}^+$ ) readily,  $\text{Cl}^-$  is a weak base, that is, a poor acceptor of ( $\text{H}^+$ ).  $\text{OH}^-$  is the strongest base (accepts a proton most readily) and its conjugate acid  $\text{H}_2\text{O}$  is a weak acid (a poor proton donor). The acid in hydrochloric acid solution is  $\text{H}_3\text{O}^+$ . The base in a solution of barium hydroxide is  $\text{OH}^-$ .

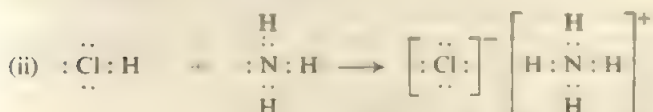
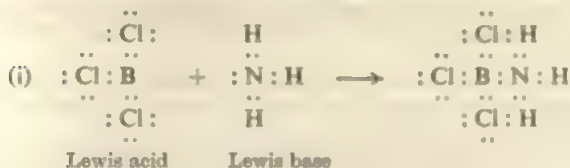
Hydrogen chloride gas and ammonium gas react in the air to form a white smoke which settles on adjacent surfaces as a white precipitate of  $\text{NH}_4\text{Cl}$ . Notice that the “dustiest” reagent bottles are the concentrated ammonia bottle and the concentrated hydrochloric acid bottle; the  $\text{HCl}$  bottle is dirtiest because the ammonia gas diffuses more rapidly. The reaction is:



(Charges are shown to indicate that the solid is ionic.) According to Arrhenius, this is not a neutralization equation, because neither  $\text{H}_3\text{O}^+$  nor  $\text{OH}^-$  is involved. Because an ( $\text{H}^+$ ) is transferred, it is a “Brønsted-Lowry” neutralization.

3. The Brønsted-Lowry Concept limits the term acid to substances that possess hydrogen. The *Lewis Concept*, introduced by G. N. Lewis the same year that Brønsted presented his idea, recognizes that other

compounds act similarly to acids when water is not present and should be called acids. For example, boron trichloride reacts with ammonia gas just as does hydrogen chloride gas.

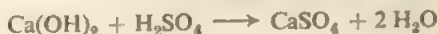


In both reactions, the base contributes electrons for sharing with the acid or a fragment of an acid.

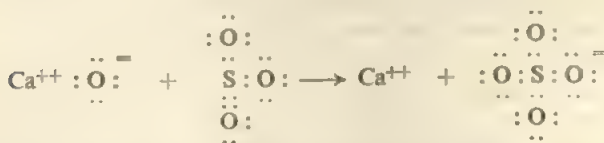
Lewis's definitions are:

- An *acid* is an ion or molecule that can accept electrons for covalent bond formation.
- A *base* is an ion or molecule that can donate a pair of electrons for covalent bond formation.
- Neutralization* is the formation of the coordinate covalent bond.

These definitions include a reaction long considered an acid-base reaction by geologists and metallurgists, but not included in the other theories because the reactants are not the hydroxide and hydronium ions and no proton is transferred. This reaction is acid-base by all theories:



but the reaction of the anhydrides is acid-base only according to the Lewis Theory:



The oxide is the base, because the oxide ion contributes the 2 electrons for the covalent bond. Sulfur trioxide is the acid, because it accepted the pair of electrons for sharing.

The Lewis Concept is more inclusive than the Brønsted-Lowry Theory. Because most acid-base reactions appearing in this text take place in water solutions, for which the Brønsted-Lowry definition is sufficient, they will be discussed in terms of that concept.

## EXERCISES—Set I

1. State Arrhenius's Theory of Electrolytic Dissociation.
2. Which types of electrolytes are ionized when dissolved in water? Which types are simply dissociated?
3. Three different solutions containing equal number of moles of solute in the same weight of water freeze at these temperatures:  $-0.42$ ,  $-0.50$  and  $-0.84$ . What kinds of substances might these solutes be?
4. What ions conduct current when a dilute solution of sulfuric acid is electrolyzed?
5. Name four properties of solutions of electrolytes that distinguish them from solutions of non-electrolytes.
6. Why is the precipitation of silver metal on a copper wire immersed in a silver nitrate solution a slower reaction than the precipitation of silver chloride accomplished by mixing solutions of silver nitrate and sodium chloride?
7. Name two tests one might use to distinguish a weak electrolyte from a strong electrolyte.
8. Name five different types of ionic reactions. Write a net ionic equation to represent each type.
9. What does a net ionic equation show?
10. Why are overall equations useful?
11. What is a spectator ion?
12. How are each of the following written when appearing in net ionic equations: (a) dilute sulfuric acid, (b) dilute hydrochloric acid, (c) acetic acid, (d) sulfurous acid, (e) ammonia solution, (f) oxalic acid, (g) calcium hydroxide solution, (h) sodium chloride solution, (i) precipitate of barium sulfate, (j) copper metal, (k) elemental sulfur?
13. What color is litmus paper in an acid solution? What color is phenolphthalein in acid solution?
14. Why is the base usually titrated into the acid solution when phenolphthalein is the indicator?
15. Why cannot the conductometric apparatus be used to indicate the neutralization point (end point) when ammonia solution is titrated into hydrochloric acid solution?
16. In what sense is  $1/2$  mole of  $\text{H}_2\text{SO}_4$  equivalent to 1 mole of  $\text{HCl}$ ? to one mole of ammonia?
17. Name three polyprotic acids.
18. Write three definitions of a base.
19. Why is the Brønsted-Lowry Concept more general than the Arrhenius Concept?
20. Hydrocyanic acid is a weaker acid than acetic acid. How do the acetate ion ( $\text{OAc}^-$ ) and the cyanide ion ( $\text{CN}^-$ ) compare in strength as bases?

## EXERCISES—Set II

Write the following in *balanced net ionic form*:

1.  $\text{NaOH} + \text{HCl} \longrightarrow \text{NaCl} + \text{H}_2\text{O}$
2.  $\text{Ca}(\text{OH})_2 + \text{HCl} \longrightarrow \text{CaCl}_2 + \text{H}_2\text{O}$
3.  $\text{HOAc} + \text{Ca}(\text{OH})_2 \longrightarrow \text{Ca}(\text{OAc})_2 + \text{H}_2\text{O}$
4.  $\text{HOAc} + \text{NaOH} \longrightarrow \text{NaOAc} + \text{H}_2\text{O}$
5.  $\text{H}_2\text{S} + \text{NH}_3 \longrightarrow (\text{NH}_4)_2\text{S}$
6.  $\text{H}_2\text{S} + \text{NaOH} \longrightarrow \text{Na}_2\text{S} + \text{H}_2\text{O}$
7.  $\text{HCl} + \text{NH}_3 \longrightarrow \text{NH}_4\text{Cl}$
8.  $\text{AgNO}_3 + \text{NaCl} \longrightarrow \text{AgCl}_{(s)} + \text{NaNO}_3$
9.  $\text{BaCl}_2 + \text{Na}_2\text{SO}_4 \longrightarrow \text{BaSO}_{4(s)} + \text{NaCl}$
10.  $\text{Cu}(\text{NO}_3)_2 + \text{H}_2\text{S} \longrightarrow \text{CuS}_{(s)} + \text{HNO}_3$
11.  $\text{Ca}(\text{HCO}_3)_2 \longrightarrow \text{CaCO}_{3(s)} + \text{H}_2\text{O} + \text{CO}_2$
12.  $\text{Cl}_2 + \text{NaBr} \longrightarrow \text{Br}_2 + \text{NaCl}$
13.  $\text{AgCl}_{(s)} + \text{NH}_3 \longrightarrow \text{Ag}(\text{NH}_3)_2\text{Cl}$
14.  $\text{Br}_2 + \text{NH}_4\text{I} \longrightarrow \text{NH}_4\text{Br} + \text{I}_2$
15.  $\text{F}_2 + \text{H}_2\text{O} \longrightarrow \text{HF} + \text{O}_2$



16.  $\text{Na} + \text{H}_2\text{O} \longrightarrow \text{NaOH} + \text{H}_2$
17.  $\text{Zn} + \text{Cu}(\text{NO}_3)_2 \longrightarrow \text{Zn}(\text{NO}_3)_2 + \text{Cu}$
18.  $\text{Al} + \text{CuCl}_2 \longrightarrow \text{AlCl}_3 + \text{Cu}$
19.  $\text{Ba}(\text{OH})_2 + \text{Na}_2\text{SO}_4 \longrightarrow \text{BaSO}_4 + \text{NaOH}$
20.  $\text{HNO}_3 + \text{Ba}(\text{OH})_2 \longrightarrow \text{Ba}(\text{NO}_3)_2 + \text{H}_2\text{O}$

### PROBLEMS

1. 22.4 L of a pure gas at STP is dissolved in 2000 g of water. The freezing point of the solution is  $-1.86^\circ\text{C}$ . Is the solute gas a non-electrolyte or an electrolyte?
2. 7.1 g of  $\text{Na}_2\text{SO}_4$  is dissolved in 200 g of water. Calculate:
  - a. the freezing point of the solution
  - b. the boiling point of the solution
  - c. the vapor pressure at  $80^\circ\text{C}$
  - d. the osmotic pressure at  $25^\circ\text{C}$
3. A quantity of salt ( $\text{NaCl}$ ) was spilled into 200 ml of water. The resulting solution boiled at  $100.30^\circ\text{C}$ . How much salt was spilled?
4. Calculate the molecular and equivalent weights of each of the following acids and bases:
 

a. $\text{HCl}$	d. $\text{H}_3\text{C}_2\text{O}_4$	g. $\text{Ca}(\text{OH})_2$
b. $\text{HOAc}$ ( $\text{CH}_3\text{COOH}$ )	e. $\text{NaOH}$	h. $\text{Al}(\text{OH})_3$
c. $\text{H}_3\text{PO}_4$	f. $\text{Ba}(\text{OH})_2$	i. $\text{NH}_3$
5. How many grams of solute are contained in 1 liter of:
 

a. 1 M $\text{HCl}$	e. 0.23 N $\text{Ca}(\text{OH})_2$
b. 1 N $\text{HCl}$	f. 1.29 M $\text{Ba}(\text{OH})_2$
c. 1.5 M $\text{H}_2\text{SO}_4$	g. 0.63 N $\text{H}_3\text{PO}_4$
d. 1.5 N $\text{H}_2\text{SO}_4$	
6. How many grams of solute are there in:
 

a. 2500 ml of 1.8 N $\text{H}_2\text{SO}_4$	d. 3.2 L of 0.8 N $\text{NaOH}$
b. 280 ml of 0.15 N $\text{Ba}(\text{OH})_2$	e. 0.75 L of 6.4 N $\text{HCl}$
c. 954 ml of 0.89 N $\text{H}_3\text{PO}_4$	
7. How many ml of the following solutions can be made from 100 g of the solute:
 

a. 1 M $\text{H}_2\text{C}_2\text{O}_4$	d. 0.012 M $\text{Ca}(\text{OH})_2$
b. 3 M $\text{H}_2\text{C}_2\text{O}_4$	e. 0.012 N $\text{Ca}(\text{OH})_2$
c. 2.4 N $\text{H}_2\text{C}_2\text{O}_4$	
8. What is the molarity of each:
 

a. 2.4 N $\text{HCl}$	d. 6.0 N $\text{HOAc}$
b. 0.38 N $\text{H}_2\text{SO}_4$	e. 0.03 N $\text{H}_2\text{C}_2\text{O}_4$
c. 12.1 N $\text{HNO}_3$	
9. What is the normality of each:
 

a. 3.6 M $\text{HNO}_3$	d. 2.4 M $\text{H}_3\text{PO}_4$
b. 0.29 M $\text{H}_2\text{SO}_4$	e. 0.58 M $\text{HCN}$
c. 0.36 M $\text{H}_2\text{C}_2\text{O}_4$	
10. Write a general rule relating the normality to the molarity of solutions.
11. Calculate the normality of the solutions made as indicated below:
  - a. 100 ml of 1.8 N  $\text{HCl}$  is diluted with water to 200 ml
  - b. 100 ml of 2.9 N  $\text{HCl}$  is diluted to 250 ml
  - c. 150 ml of 0.54 N  $\text{H}_2\text{SO}_4$  is diluted to 450 ml
  - d. 320 ml of 1.6 M  $\text{H}_2\text{SO}_4$  is diluted to 684 ml
  - e. 1.2 L of 0.32 M  $\text{H}_2\text{C}_2\text{O}_4$  is diluted to 4.80 L
  - f. 200 ml of 2 M  $\text{H}_2\text{SO}_4$  is added to 300 ml of 4 N  $\text{H}_2\text{SO}_4$
  - g. 300 ml of 2.4 M  $\text{H}_2\text{SO}_4$  is added to 250 ml of 2.4 N  $\text{H}_2\text{SO}_4$
12. Calculate the normality of each of the following solutions for which no concentration is given:
  - a. 20 ml of  $\text{NaOH}$  is neutralized by 30 ml of 2 N  $\text{HCl}$
  - b. 13,400 ml of  $\text{Ca}(\text{OH})_2$  is neutralized by 10.0 ml of 1.2 N  $\text{H}_2\text{SO}_4$
  - c. 25 ml of 3.0 M  $\text{H}_2\text{SO}_4$  is neutralized with 35 ml of  $\text{NaOH}$
  - d. 11.2 ml of 2.6 N  $\text{HOAc}$  is neutralized with 341 ml of  $\text{Ba}(\text{OH})_2$
  - e. 290 ml of  $\text{HOAc}$  solution neutralized 20 g of  $\text{NaOH}$  dissolved in 100 ml of water
  - f. 10 ml of 0.261 N  $\text{H}_2\text{SO}_4$  is dissolved in 100 ml of water and then neutralized with 13.5 ml of  $\text{NaOH}$

SULFUR AND RELATED  
ELEMENTS

## 1. HISTORY

Sulfur is an interesting element. Although it has been known for at least 4,000 years, it has been used widely for less than 200 years. For many years the island of Sicily was the chief source of sulfur. The Egyptians southeast of Sicily used sulfur for bleaching cotton as early as 2000 B.C. Egyptian paintings dating from 1600 B.C. contain a pigment made of bright yellow sulfur. In Homeric times, sulfur was used as a fumigant and a purifier. Romans used sulfur in finishing cast bronze, in medicines, as a fumigant and in finishing cloth. Records indicate that the early Britains were acquainted with the element. It was probably brought to them by their Roman conquerors, from whom came the common name "brimstone," a variation of "bryn stone" ("the stone that burns"). However, sulfur was not identified as an element until 1810, several years after one of its compounds, sulfuric acid, was a recognized commercial product. Only 575,000 tons of sulfur were produced in 1900, but by 1956, 7,600,000 tons were produced, and the need was rapidly increasing. In 1900, Sicily was the major producer; the United States produced not more than 3,000 tons. Today the United States produces more than 90 per cent of the world's supply.

## 2. OCCURRENCE

Sulfur occurs free in nature and also as sulfides and sulfates. The more common sulfides are pyrite ( $\text{FeS}_2$ ); chalcocite ( $\text{Cu}_2\text{S}$ ), a major copper ore; chalcopyrite ( $\text{CuFeS}_2$ ); sphalerite ( $\text{ZnS}$ ), a zinc ore; galena ( $\text{PbS}$ ), a lead ore, and bornite ( $\text{Cu}_5\text{FeS}_4$ ). The commonly occurring sulfates are gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ); anhydrite ( $\text{CaSO}_4$ ); kieserite ( $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ ) and anglesite

( $\text{PbSO}_4$ ). Elemental and combined sulfur occur in coal and petroleum. One commercial source of sulfur is the hydrogen sulfide that is present as a noxious impurity in "sour" natural gas.

*Sulfur is the fifteenth element in abundance in the earth's crust, comprising an estimated 0.06% of the total weight. It is also found in plant and animal tissue; it is the eighth most abundant element in the human body, making up 0.25% of the total weight.*

Native or elemental sulfur occurs in many places. It often occurs in volcanic regions, encrusted on the walls and vents of craters. Volcanic areas containing sulfur exist in Japan, Chile, Mexico, Iceland, Norway and Spain.

An interesting story concerns the presence of sulfur deposits on volcanic crater walls. While Cortez was conquering Mexico in the middle of the sixteenth century, his army ran short of gun powder. Black powder may be made of charcoal, saltpeter and sulfur. Supplies of the first two were available, but sulfur was not to be had. One soldier, Francisco Montano, had himself lowered in a basket 400 to 500 feet into the crater of Popocatepetl where he scraped sufficient sulfur for their needs.

Native sulfur deposits, more important than those in volcanic areas, accompany gypsum and anhydrous calcium sulfate accumulations. The major deposits are found in the Texas-Louisiana-Mexico area and in Sicily. 95% of all sulfur produced is derived from these deposits.

### 3. PRODUCTION OF SULFUR

#### A. ANCIENT METHOD

Sulfur is produced in Sicily by melting the native sulfur from the ore—much the same method as was used in ancient times. The ore is near the surface. It is moved by hand or mechanical shovels and dumped into a huge masonry furnace about 100 feet in diameter and 35 feet high. The charge is ignited about 12 feet above the bottom. One third of the sulfur burns, melting the rest from the sulfate rock. The sulfur trickles down through the ore charge to the floor of the furnace, then out a vent where it is run into wooden molds. The ancients looked upon the burning of sulfur with its blue flame and acrid odor as a terrible thing. The worst judgment one could obtain was assignment to a "lake of fire and brimstone."

#### B. FRASCH PROCESS

But in the Texas-Louisiana area, which yields 90 per cent of all the sulfur produced, the sulfur, mixed with calcium sulfate rock, lies between 500 and 3000 feet from the surface, in salt domes thrust up by underlying columns of salt (Fig. 18.1). The first salt-sulfur dome was discovered in 1869 in an oil well-drilling operation. Various attempts were made to sink mines by conventional methods, but all failed. An engineer, D. Herman Frasch, conceived a plan to melt the sulfur underground and force it up as a liquid.

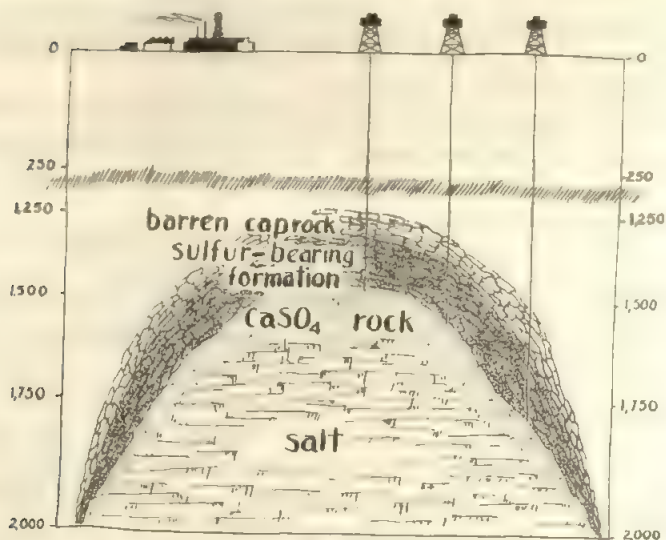


Figure 18.1. Free sulfur deposits.

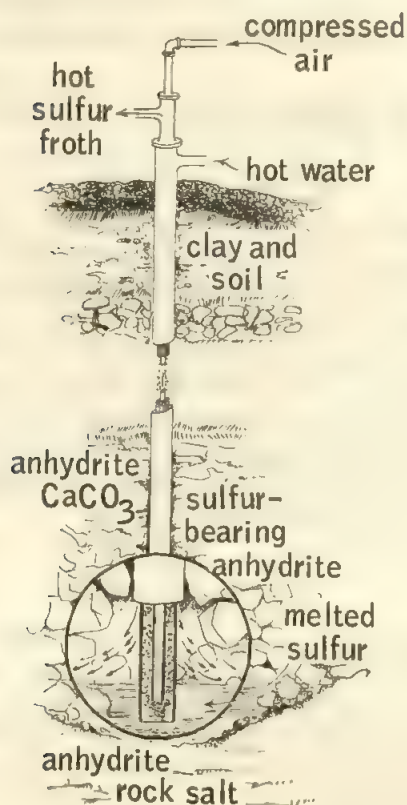


Figure 18.2. Sulfur well.



After 10 years of trial, he was successful. The Frasch Process has made the United States the chief supplier of sulfur.

In the Frasch Process the sulfur is melted by superheated water and raised with an air lift. Sulfur melts at about  $113^{\circ}\text{C}$  (which is above the boiling point of water). However, by placing the water under a pressure of 100 pounds per square inch (nearly seven atmospheres) the temperature can be raised to  $170^{\circ}\text{C}$  without boiling. The installation is a well of three concentric pipes (Fig. 18.2). The outermost pipe reaches to the bottom of the sulfur-bearing stratum. It is perforated through the sulfur layer so that hot water may pass out to melt the sulfur and the melted sulfur can enter and stand in the next inner pipe. Compressed air is forced down the innermost pipe, which does not quite reach the bottom of the well. The air rises up through the second pipe carrying a mixture of melted sulfur, water and froth. At the surface the liquid mixture is de-aerated and flooded into huge vats formed by temporary nesting walls and the sulfur cools, hardens and dries. As the mound of hardened sulfur rises, the nesting walls are raised until mountains about 375 feet long, 200 feet wide and 30 feet high are formed. When needed, the sulfur is blasted from the face of the mound and loaded by power shovel into railroad cars. The sulfur from the Frasch Process is 99.05% pure, probably the purest product mined, except gold dust. Over 9,000,000 tons of sulfur were extracted from the first salt dome worked by the Frasch Process.

### C. FROM NATURAL GAS

The gaining of sulfur from "sour" natural gas is an interesting process. The hydrogen sulfide, absorbed in and then distilled from a solution of an alkyl amine, is partially burned:



The moist mixture of unchanged  $\text{H}_2\text{S}$  and  $\text{SO}_2$  is cooled and, with catalysis, reacts to form sulfur:



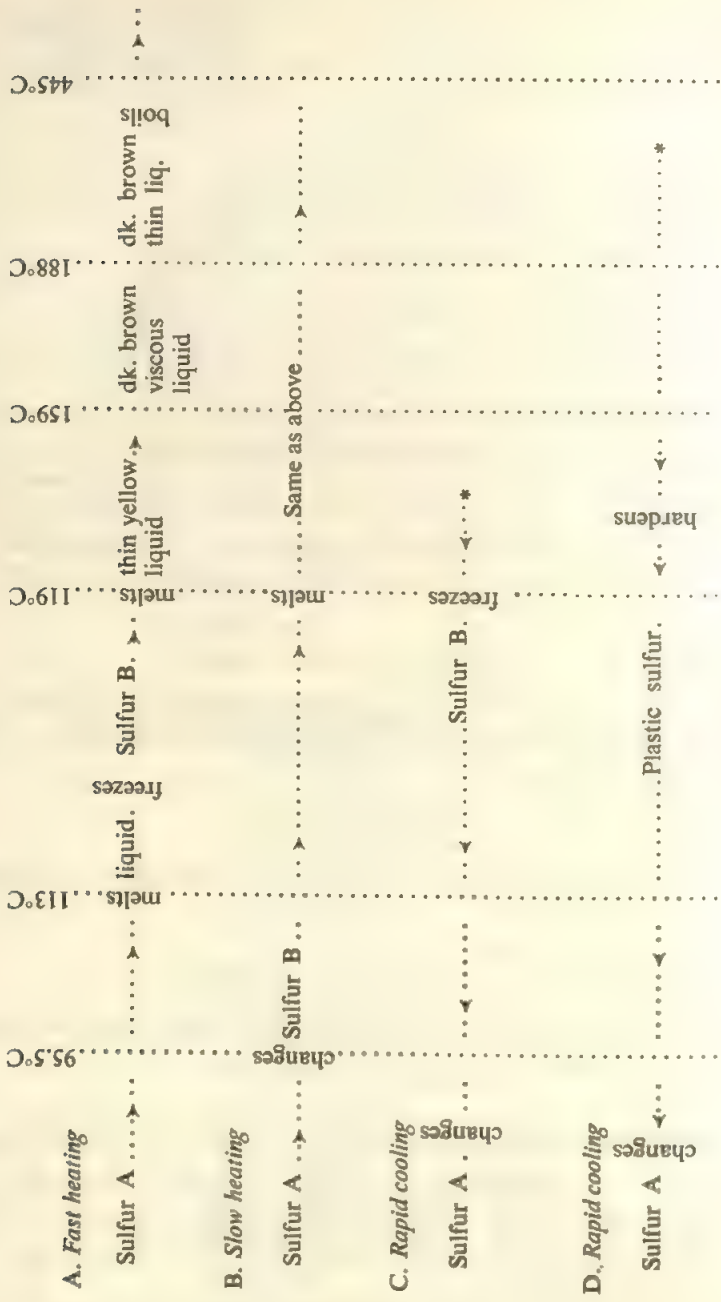
The sulfur vapor is condensed and collected in molten sulfur. Sulfur from these sources may be further purified by sublimation.

## 4. THE PHYSICAL PROPERTIES OF SULFUR; ALLOTROPY

Pure sulfur as obtained from chemical companies is a bright yellow, tasteless and odorless solid with a density double that of water—2.07 g/ml. It is insoluble in water, but quite soluble in carbon disulfide (about 34 per cent at room temperature).

Certain observations obtained by heating and cooling sulfur are interesting.

A. When solid sulfur is heated rapidly, it melts at  $112.8^{\circ}\text{C}$  to form a thin, straw-colored liquid with a density of 1.80 g/ml. As heating continues



and at no set temperature, crystallization may occur, forming bright yellow needles. They melt in turn at  $119.25^{\circ}\text{C}$  to give the same straw-colored, mobile liquid. As the temperature rises, little change is noted in the liquid sulfur, although the color darkens slightly and both the density and viscosity of the free-flowing liquid decrease steadily. At  $159^{\circ}\text{C}$  a marked change begins to take place. The liquid darkens and the viscosity increases rapidly until at  $188^{\circ}\text{C}$  the now dark brown liquid is so viscous one cannot pour it from the container. As the temperature rises beyond  $188^{\circ}\text{C}$ , the viscosity drops rapidly, but not so rapidly as it increased between  $159$  and  $188^{\circ}\text{C}$ . The color remains with rising temperature. At  $444.6^{\circ}\text{C}$ , the thin, free-flowing but dark brown liquid has a vapor pressure of 1 atmosphere and it boils.

- B. When sulfur is heated *very, very* slowly, a change occurs at  $95.5^{\circ}\text{C}$ . The solid changes completely to the needle-type sulfur. No change occurs with continued heating until the needles melt as before at  $119.25^{\circ}\text{C}$ . The liquid obtained behaves exactly as described above.
- C. When liquid sulfur between  $112.8^{\circ}\text{C}$  and  $159^{\circ}\text{C}$  is cooled quickly, it crystallizes to give needle-shaped crystals, which gradually change at room temperature to a solid with the same properties as the original sample.
- D. When liquid sulfur between  $188^{\circ}\text{C}$  and the boiling point is cooled rapidly to room temperature, a brown rubbery material called plastic sulfur is obtained. Plastic sulfur gradually changes to the original bright yellow sulfur.

The four experiments are represented on page 266.

The unusual changes in state noted above might be explained partially on the basis of structure. Sulfur A is rhombic sulfur, so named because the crystals are orthorhombic (Fig. 18.3a). Sulfur B is monoclinic sulfur because of its crystal habit (Fig. 18.3b). Both solids contain  $\text{S}_8$  molecules, but they are packed together differently (Fig. 18.4a,b). The exact packing arrangement is not known. Rhombic sulfur is stable up to  $95.5^{\circ}\text{C}$ ; monoclinic sulfur is stable between  $95.5^{\circ}\text{C}$  and its melting point  $119.25^{\circ}\text{C}$ . However, the change from one crystal habit to the other is slow because of the difficulty the  $\text{S}_8$  molecules experience in moving in the solid. Therefore, when rhombic sulfur is heated rapidly, the change to monoclinic does not occur, and the unstable rhombic sulfur melts at its own melting point— $112.8^{\circ}\text{C}$ —only to freeze to the stable monoclinic sulfur and to melt again. The unusual increase in viscosity of the liquid sulfur when heated from  $159^{\circ}\text{C}$  to  $188^{\circ}\text{C}$  occurs because the  $\text{S}_8$  rings break open with greater energy of vibration and join together to form long chains, some as long as 10,000 atoms. The change from nearly spherical  $\text{S}_8$  molecules, which roll easily over one another, to tangled chains accounts for the great increase in viscosity. As the temperature rises above  $188^{\circ}\text{C}$ , the natural increase in vibrational movement allows the chains to slide more easily past one another, and the viscosity decreases as expected. When cooled rapidly, the chains do not break rapidly enough, no orderly pattern can be assumed by the odd-sized molecules, and plastic sulfur results (Fig. 18.4c), only

to change in time to the stable rhombic form. Approximately one-third of the atoms in dark viscous sulfur are in chains; the rest remains in  $S_8$  molecules. However, that fraction is sufficient to contribute the unusual properties.

The existence of two or more different forms of a solid, stable over different temperature ranges, is known as *allotropy*. Rhombic, monoclinic and plastic

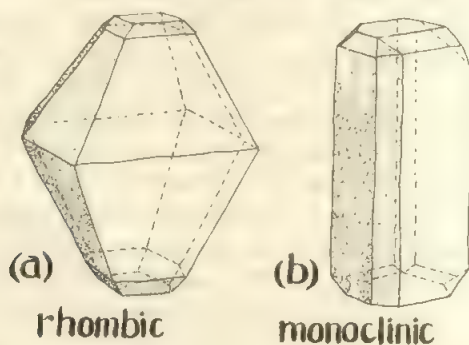


Figure 18.3. Sulfur crystals.

sulfur are allotropes. The phenomenon is also known as polymorphism (many forms). Rhombic and monoclinic sulfur are polymorphs; plastic sulfur is described as amorphous (having no form). Allotropy is a rather general phenomenon of both elements and compounds. Ice has five other forms, each of which is more dense than water. Tin has two stable forms; iron, three. Selenium, and tellurium (in Group VI with sulfur) and phosphorus, arsenic, antimony and bismuth have more than one stable form. Some allotropes differ in kinds of molecules. Others, such as monoclinic and rhombic sulfur, differ only in the pattern of the molecules in the crystal.

Table 18.1. Density and Molecular Composition of Sulfur Vapor

Temperature $^{\circ}C$	Density g/L	Molecular Weight	Molecules Present
444.6	3.650	215.0	$S_8$ , $S_6$ and $S_2$
600.0	1.900	137.0	$S_8$ , $S_6$ , $S_2$
800.0	0.729	64.4	$S_2$
1000.0	0.614	64.2	$S_2$

Table 18.1 shows the density of sulfur vapor at the boiling point and at three higher temperatures, all at 1 atmosphere pressure. Included are calculated molecular weights (from gas density) and the corresponding molecular composition of the vapor. At the boiling point, the vapor has a



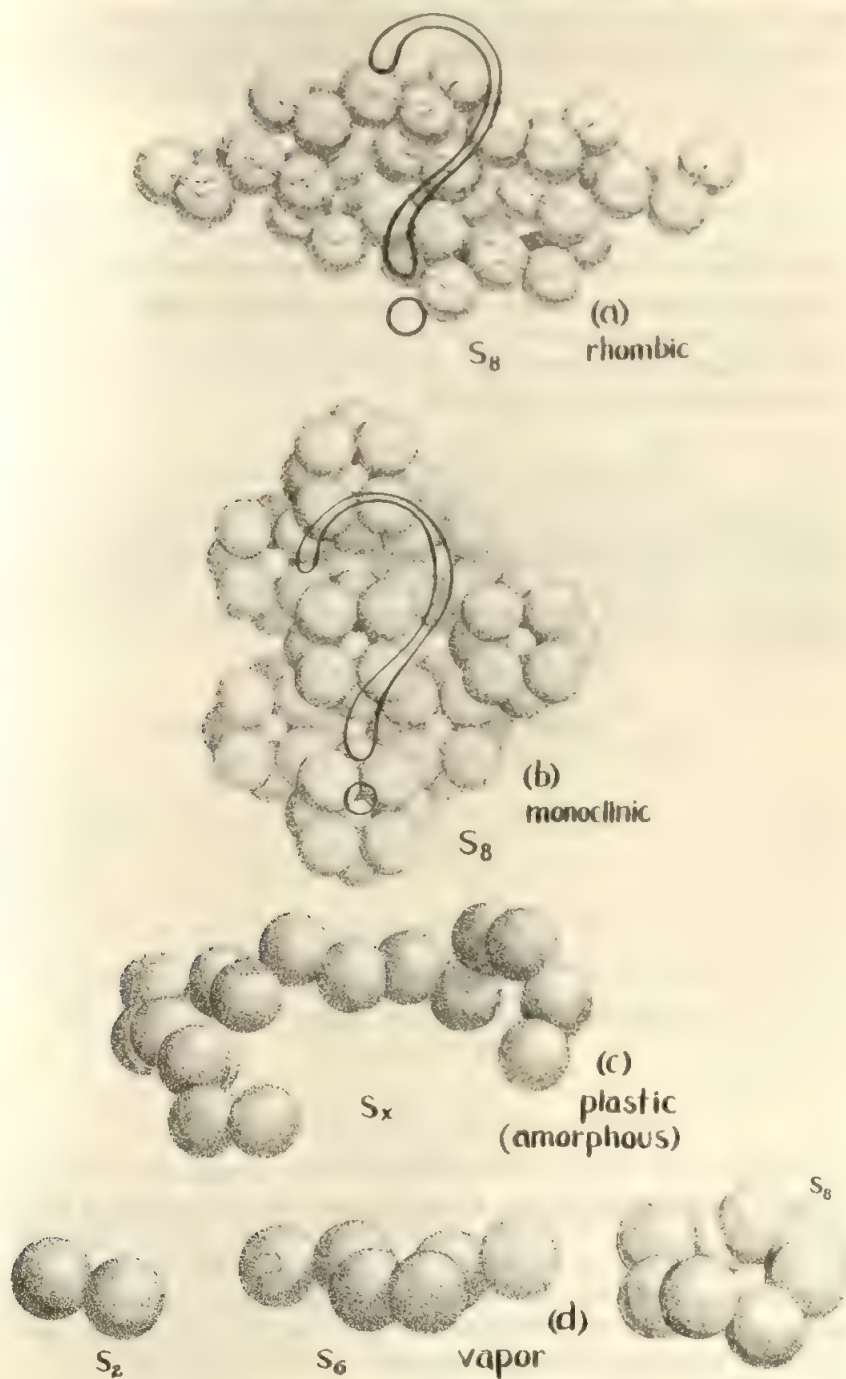


Figure 18.4. Sulfur molecules.

calculated molecular weight of 215, corresponding to a formula of  $S_{6.7}$ . Obviously the vapor is mostly  $S_8$ , with some  $S_6$  and  $S_2$  (Fig. 18.4d). As the temperature rises, the  $S_8$  rings are opened and broken, until at  $1000^\circ\text{C}$  only  $S_2$  molecules remain.

### 5. USES OF SULFUR

Sulfur has many uses. (1) Eighty per cent of the sulfur produced is used in making sulfuric acid, which is employed in a great many processes. (Some will be discussed later.) (2) The other 20 per cent is used in treating pulp for all types of paper: in making carbon disulfide, cellophane, rayon, dyestuffs, insecticides and explosives; in bleaching, in vulcanizing rubber, in leather processing and in many other ways. Thirty-five pounds of sulfur are required in the manufacture of each automobile.

### 6. CHEMICAL PROPERTIES OF SULFUR

Sulfur appears as the second member of Group VI of the Periodic Table (Table 18.2). Oxygen is the first member. Selenium, tellurium and polonium follow sulfur. Polonium is a very rare radioactive element occurring as a disintegration product of uranium and other radioactive elements. Not a great deal of its chemistry is known.

Table 18.2. Periodic Table

																		H	He
Li	Be																	F	Ne
Na	Mg																	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se			Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te			I	Xe
Cs	Ba	La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po			At	Rn
Fr	Re	Ac-Lw																	

Members of the group are not so closely related to each other as are the elements in the halogen family. Properties vary from the typical and active non-metals, oxygen and sulfur, to tellurium, with its metallic character. Oxygen is more reactive than sulfur, but sulfur and selenium (and often tellurium) reactions are similar. Each element has 6 valence electrons and can therefore either gain 2 electrons or share electrons in bonding. Two series of parallel compounds of oxygen and sulfur appear in Table 18.3.

The presence of 6 valence electrons in the sulfur atom  $(\cdot \ddot{\text{S}} \cdot)$  enables it to form the chains or rings shown in Figure 18.4a,b,c,d. It need gain only 2

electrons by sharing to have an octet configuration. Notice that at high temperature, the vapor contains  $S_2$  molecules analogous to  $O_2$  gas, but at lower temperature  $S_8$  rings persist.

**Table 18.3. Sulfur and Oxygen Compounds**

Oxygen	$H_2O$	$CO_2$	$FeO$	$ZnO$	$Na_2O$	$NaOH$	$As_2O_3$
	Water	Carbon dioxide	Ferrous oxide	Zinc oxide	Sodium oxide	Sodium hydroxide	Arsenious oxide
Sulfur	$H_2S$	$CS_2$	$FeS$	$ZnS$	$Na_2S$	$NaSH$	$As_2S_3$
	Hydrogen sulfide	Carbon disulfide	Ferrous sulfide	Zinc sulfide	Sodium sulfide	Sodium hydrosulfide	Arsenious sulfide

## 7. COMPOUNDS OF SULFUR

Sulfur exists in four common oxidation states (Table 18.4).

**Table 18.4. Oxidation States of Sulfur**

-2	$H_2S$ , hydrogen sulfide gas $ZnS$ , zinc sulfide $FeS$ , ferrous sulfide
0	Elemental, $S_8$
+4	$SO_2$ , sulfur dioxide $H_2SO_3$ , hydrogen sulfite, sulfurous acid $CaSO_3$ , calcium sulfite
+6	$SO_3$ , sulfur trioxide $H_2SO_4$ , hydrogen sulfate, sulfuric acid $CaSO_4$ , calcium sulfate

The compounds of sulfur will be studied in the order of increasing oxidation states.

### A. OXIDATION STATE OF -2

Hydrogen sulfide ( $H_2S$ ) is a gas. It boils at  $-60^\circ C$ . It has a very objectionable odor (similar to that of rotten eggs), which may be detected in concentrations as low as 10 parts per billion in air. Hydrogen sulfide is very poisonous, but its odor, which is unbearable much below lethal concentrations, serves as a warning.

*Hydrogen sulfide may be prepared:*

(1) by bubbling hydrogen gas through boiling sulfur:



but the yield is not good.

(2) by the reaction of sulfides of medium active metals with an acid.

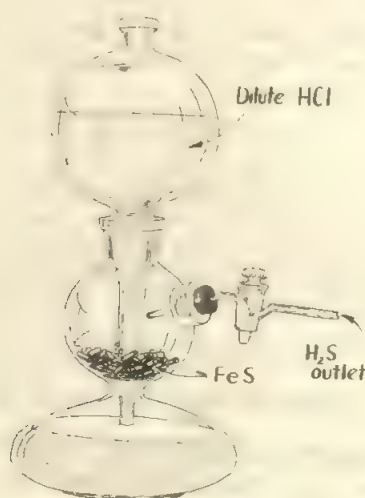
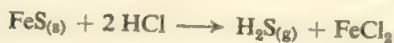
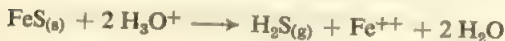


Figure 18.5. Kipp generator.

Ferrous sulfide reacts with dilute hydrochloric acid:



The net ionic equation for the reaction is:



This reaction can be carried out in a Kipp generator, an old but ingenious apparatus (Fig. 18.5). Pieces of iron sulfide rod are placed on the tray in the lower portion of the generator. With the stopcock closed, dilute hydrochloric acid is poured down the funnel. The pressure keeps the acid level below the iron sulfide, and no reaction occurs. When  $\text{H}_2\text{S}$  gas is wanted, the stopcock is opened, releasing the pressure in the lower chamber and allowing the acid to rise up to cover the iron sulfide. The  $\text{H}_2\text{S}$  formed leaves through the stopcock. To stop the reaction, the stopcock is closed. The gas generated builds up pressure, forcing the acid level down below the sulfide again. When more  $\text{H}_2\text{S}$  gas is needed, one merely opens the stopcock and repeats the procedure. Being able to turn off  $\text{H}_2\text{S}$  gas is almost as important as being able to prepare it.



- (3) by heating a paraffin sulfur mixture. In practice the molten sulfur-paraffin mixture is poured on asbestos to keep it from hardening in one piece. The asbestos-sulfur-paraffin mixture can be heated when  $\text{H}_2\text{S}$  is needed.

#### REACTIONS AND USES OF HYDROGEN SULFIDE

- (1) Hydrogen sulfide burns readily in air to give sulfur dioxide and water:



- (2) Hydrogen sulfide reacts with sulfur dioxide on a moist surface to produce sulfur:



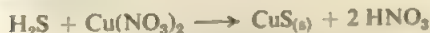
Reactions 1 and 2 are those used to convert hydrogen gas from sour natural gas to sulfur. Equation 2 represents the reaction occurring on the walls of cooling volcanos. Two of the escaping gases, hydrogen sulfide and sulfur dioxide, react as they come together on the moist walls.

- (3) Hydrogen sulfide is a weak acid. It dissolves sparingly in water to form a solution about 0.1 molar. It is a diprotic acid, ionizing in this manner:

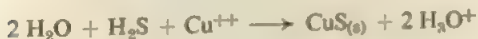


Because of the two available hydrogens, the acid, even though it is very weak, has just as great a capacity per mole in neutralization as does sulfuric acid.

- (4) Several metals have very insoluble sulfides.  $\text{H}_2\text{S}$  may be used as a source of sulfide ions to precipitate the metal ions from solution for identification. One of these metals is copper. When hydrogen sulfide is bubbled into a solution of copper nitrate, the following reaction occurs:

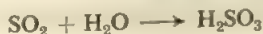


The net ionic equation is:



#### B. OXIDATION STATE OF +4

Sulfur dioxide ( $\text{SO}_2$ ) is the most important compound containing sulfur with an oxidation state of +4. Its importance rests in the fact that it is an intermediate in the preparation of sulfuric acid. This will be discussed later in the chapter. It is the anhydride of sulfurous acid, a weak acid:



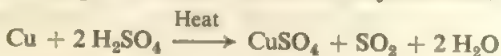
*Sulfur dioxide may be prepared:*

- (1) *by burning sulfur in air, it is prepared by this method at the rate of a few million tons per year.*
- (2) *by burning iron pyrites and other metal sulfides:*

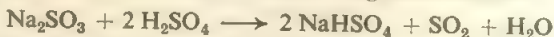


This reaction occurs as a side reaction in the smelting of sulfide ores. The sulfur dioxide is scrubbed from the smoke stack gases and converted to sulfuric acid.

- (3) *by heating an inactive metal with sulfuric acid:*



- (4) *by treating sulfite salts with a strong acid solution:*



These last two preparations (3) and (4) are useful only in the laboratory. Again, practically all the sulfur dioxide produced is used in making sulfuric acid.

### C. OXIDATION STATE OF +6

Sulfur trioxide ( $\text{SO}_3$ ) is a colorless liquid which freezes at  $15^\circ\text{C}$ , boils at  $46^\circ\text{C}$  and has a biting odor. The volatile liquid has a great attraction for

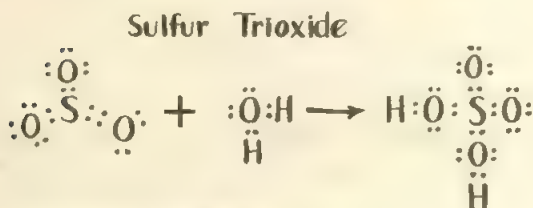


Figure 18.6. Hydration of sulfur trioxide.

water. Several different compounds of sulfur trioxide and water are known. All are liquids at room temperature. The formula of some are shown below:

$(\text{SO}_3)_2 \cdot \text{H}_2\text{O}$	$\text{SO}_3 \cdot \text{H}_2\text{O}$	$\text{SO}_3 \cdot 2 \text{H}_2\text{O}$	$\text{SO}_3 \cdot 7 \text{H}_2\text{O}$
$\text{H}_2\text{S}_2\text{O}_7$	$\text{H}_2\text{SO}_4$	$\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$	$\text{H}_2\text{SO}_4 \cdot 6 \text{H}_2\text{O}$
Pyrosulfuric acid or fuming sulfuric acid	Sulfuric acid	Monohydrate of sulfuric acid	Hexahydrate of sulfuric acid

The formations of these compounds may account in part for the attraction of  $\text{SO}_3$  for water. All of these are formed from sulfur trioxide and water with an evolution of heat. The combination forming sulfuric acid is represented in Figure 18.6.

Sulfur trioxide is used almost exclusively for the preparation of sulfuric acid.

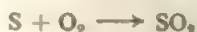
### D. SULFURIC ACID

*Sulfuric acid* ( $\text{H}_2\text{SO}_4$ ) is one of the most important of all chemicals in chemical and related industries. About 17,000,000 tons of the acid are produced each year. There are two major methods of manufacture: the contact process and the lead chamber process.

#### (1) CONTACT PROCESS

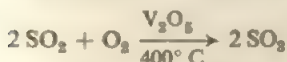
Preparation of sulfuric acid by the contact process usually starts with crude sulfur (99.05 per cent pure) from the Frasch process:

- (a) The sulfur is burned in air to give sulfur dioxide:

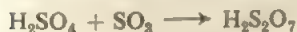


or the sulfur dioxide may be recovered from smelter gases and purified.

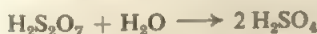
- (b) The most important step is the catalytic oxidation of sulfur dioxide to sulfur trioxide by air. The gas mixed with air is passed over a vanadium pentoxide catalyst at about 400 to 450°C. About 99% of the sulfur dioxide is converted to sulfur trioxide.



- (c) Since sulfur trioxide is the anhydride of sulfuric acid, it would seem logical that it should merely be added to water. However, mechanical problems arise. The sulfur trioxide vapor (at the temperature of addition) forms fog droplets with water vapor. The droplets diffuse slowly and the reaction comes almost to a standstill. Consequently, the sulfur trioxide vapor is dissolved in concentrated sulfuric acid to form fuming sulfuric acid:



- (d) Water is then added, converting the fuming sulfuric acid to sulfuric acid, two molecules for one.

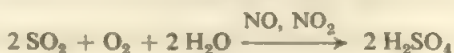


Steps (c) and (d) occur simultaneously, with water being metered into the concentrated acid as the sulfur trioxide dissolves. Pure concentrated sulfuric acid is formed this way, the solution being 98 per cent  $\text{H}_2\text{SO}_4$ . The acid is pure because the sulfur dioxide of which it is made is pure. Unless pure sulfur dioxide is passed over the catalyst, it is soon poisoned and is no longer effective.

#### (2) LEAD CHAMBER PROCESS

About 30% of the sulfuric acid used is produced by the lead chamber process. In this process, sulfur dioxide gas not pure enough to be used in the

contact process is mixed with air and the oxide gases of nitrogen ( $\text{NO}$  and  $\text{NO}_2$ ), then sprayed with water in huge lead-lined chambers. Sulfuric acid collects on the floor of the chamber.



The nitrogen oxides are catalysts. In some way, they act as carriers of oxygen, but the exact role of the catalyst mixture is complicated. The sulfuric acid gained from this process is never more than 60 or 70 per cent acid. Furthermore, it is quite impure. However, some industries, such as the fertilizer industry, can use the acid as it is. It is not economical to purify or concentrate it.

#### PROPERTIES AND USES OF SULFURIC ACID

Concentrated sulfuric acid, as sold commercially and as obtained directly from the contact process, is a thick, syrupy, colorless liquid with a boiling point of  $338^\circ\text{C}$ . It fumes slightly in moist air due to slowly escaping sulfur trioxide vapor. It has a density (1.84 g/ml) almost double that of water and is 98.3 per cent  $\text{H}_2\text{SO}_4$ . The solution is 18.4 molar in acid as shown by the following calculation:

$$1.84 \text{ g/ml} \times 1000 \text{ ml/L} = 1840 \text{ g of } \text{H}_2\text{SO}_4 \text{ and } \text{H}_2\text{O per liter}$$

$$1840 \text{ g/L} \times 0.983 = 1812 \text{ g of } \text{H}_2\text{SO}_4/\text{L}$$

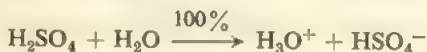
$$\frac{1812 \text{ g } \text{H}_2\text{SO}_4/\text{L}}{98 \text{ g } \text{H}_2\text{SO}_4/\text{mole}} = 18.4 \text{ moles/L} = 18.4 \text{ M}$$

The complete setup is:

$$\frac{1.84 \text{ g/ml} \times 1000 \text{ ml/L} \times 0.983}{98 \text{ g/mole}} = 18.4 \text{ M}$$

This corresponds to a normality of 36.8.

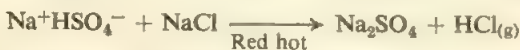
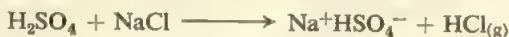
*Sulfuric acid is a strong acid.* The first ionization occurs completely when sufficient water is added:



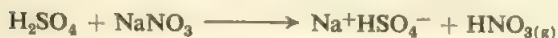
The second ionization is comparatively small:



Bisulfate ( $\text{HSO}_4^-$ ) ionizes to a greater extent than acetic acid, but it is still considered a weak acid. Because it is a strong acid, and because the boiling point is high, concentrated sulfuric acid is used for the production of two other mineral acids: hydrochloric acid and nitric acid:



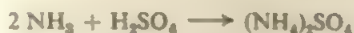
and





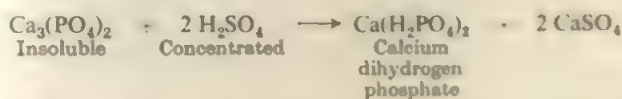
The gases  $\text{HCl}$  and  $\text{HNO}_3$  are bubbled into water. At one time these were the major preparations of the acids. Now they are being replaced by other methods.

Sulfuric acid is used to produce some fertilizers. One fertilizer, ammonium sulfate, is made simply by the reaction of ammonia solution and crude sulfuric acid:



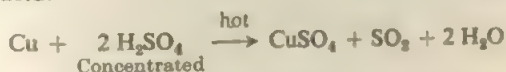
Ammonium sulfate is a water soluble plant source of nitrogen and sulfate.

Insoluble phosphate rock can be rendered soluble and available to plants with sulfuric acid:

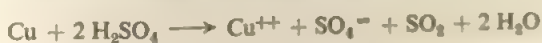


The dried mixture of the two salts is called super phosphate.

*Hot concentrated sulfuric acid is an oxidizing agent.* Copper metal will not dissolve in hydrochloric acid solution because hydrogen is above copper in the activity series. Copper will not replace the hydronium ion in solution, but the cupric ion will be replaced by the hydronium ion. However, copper metal will dissolve in hot concentrated sulfuric acid, but by reducing sulfur in sulfuric acid.



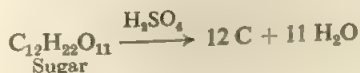
In net ionic form,  $\text{H}_2\text{SO}_4$  in concentrated sulfuric acid is written as a molecule, because there is insufficient water for ionization.



The oxidation state of copper is increased from 0 to +2 and copper is oxidized.

Sulfuric acid is used in the petroleum industry to oxidize tars and organic sulfides for removal.

Like its anhydride, sulfur trioxide, *sulfuric acid is a strong dehydrating agent*, taking up water to form further hydrates. Not only will concentrated sulfuric acid remove water from air bubbled through it, but it also will subtract the elements of water from some compounds, decomposing them. Wood is charred by sulfuric acid, largely by loss of water. Sugar is decomposed by a concentrated solution of sulfuric acid.



Water is tied up by the acid and a fluffy black residue is left behind (Fig. 18.7). Toluene and concentrated nitric acid are converted to trinitrotoluene by concentrated sulfuric acid and heat.

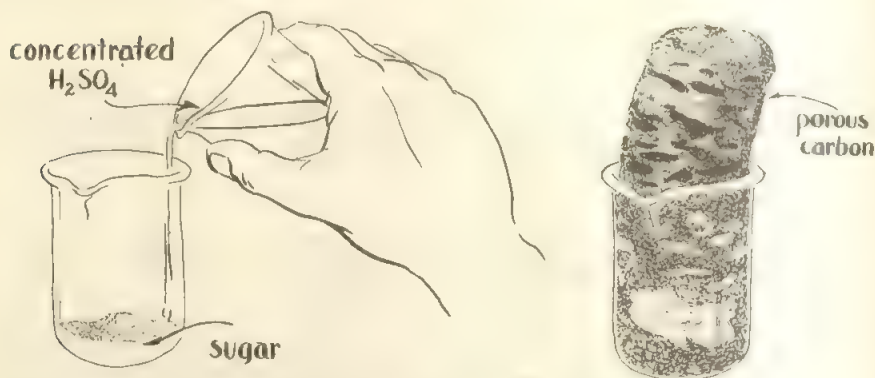
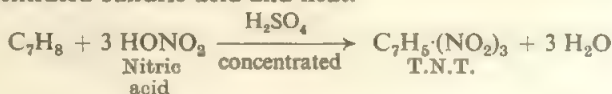
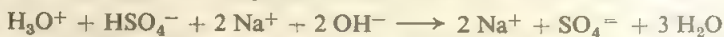


Figure 18.7. Dehydration of sugar.

### SULFATES

Sulfates are easily formed by reaction of sulfuric acid and a base:



Sodium sulfate is soluble and remains as sodium and sulfate ions in solution until the water is evaporated. Barium sulfate formed by reaction of barium hydroxide and sulfuric acid is an insoluble white solid. A slurry\* of barium sulfate is taken internally in making stomach X-rays. The solid is impenetrable by the X-rays, and therefore casts a shadow of the alimentary canal on the film.

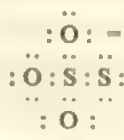
Some nearly insoluble sulfates that occur as minerals are:  $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$  (gypsum),  $\text{SrSO}_4$ ,  $\text{BaSO}_4$  and  $\text{MgSO}_4$ .

Some common sulfates are: Glauber's Salt ( $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ ), Epsom Salts ( $\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$ ), blue vitriol ( $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ ), and hydrated ferrous sulfate ( $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ ). Some double salts are: ammonium alum ( $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$ ), potassium alum ( $\text{KAl}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$  and  $\text{K}_2\text{Mg}(\text{SO}_4)_2 \cdot 6 \text{H}_2\text{O}$ ).

Sodium thiosulfate, the substance whose solution is commonly known in photography as hypo, may be considered a derivative of sodium sulfate. The structures of the sulfate and thiosulfate ions are similar:



Sulfate ( $\text{SO}_4^{2-}$ )



Thiosulfate ( $\text{S}_2\text{O}_3^{2-}$ )

\*A slurry is a thin suspension of solid in water.

In the thiosulfate ion, a sulfur atom has replaced one oxygen atom. In thiosulfate, sulfur does not have an oxidation number of  $+6$ , but of  $+2$ .

### SELENIUM AND TELLURIUM

The properties of selenium and tellurium are those expected, considering the position of the elements with respect to sulfur. The melting points and boiling points are higher than those of sulfur. They are less reactive; selenium forms many of the same type of compounds as does sulfur, and tellurium with its metallic nature forms fewer.

Sulfur is an insulator, a non-conductor of electricity; selenium is a poor conductor; and tellurium is a semiconductor. The conductivity of selenium increases 200-fold in bright light. For this reason, it is used in some photo-cells. Both elements are rare, comprising about  $10^{-7}$  per cent of the earth's crust, and therefore are much less important than sulfur.

### EXERCISES

1. How long has sulfur been known?
2. What is the origin of the term brimstone?
3. What nation is the world's chief producer of sulfur?
4. Name four compounds of sulfur that occur in natural deposits.
5. How is sulfur gained from its ore in Sicily?
6. Describe the Frasch process.
7. Why must the hot water used in the Frasch process be under pressure?
8. Is the sulfur rising from a sulfur well dissolved in water?
9. Describe how sulfur is gained from the hydrogen sulfide found in "sour" natural gas.
10. How does monoclinic sulfur differ from rhombic sulfur?
11. How might one account for the darkening in color and the increase in viscosity observed when liquid sulfur is heated above  $159^{\circ}\text{C}$ ?
12. What is the chief use of sulfur?
13. What is the ionic valence of sulfur? What are its usual oxidation states?
14. Describe one method for preparing sulfur.
15. Why are not more people poisoned by the deadly poison, hydrogen sulfide?
16. Write the equation that indicates the source of sulfur deposits on volcanic crater walls?
17. Why are several million tons of sulfur dioxide produced each year?
18. What is the source of  $\text{SO}_2$  gas in an iron smelter?
19. Why is sulfur trioxide vapor not dissolved directly in water to prepare sulfuric acid?
20. What is the oxidation state of sulfur in each of the following: (a)  $\text{S}_2\text{Cl}_2$ , (b)  $\text{SO}_2$ , (c)  $\text{SO}_4^{2-}$ , (d)  $\text{SO}_3^{2-}$ , (e)  $\text{SO}_3$ , (f)  $\text{S}_2\text{O}_3^{2-}$ , (g)  $\text{S}_2\text{O}_4^{2-}$ , (h)  $\text{H}_2\text{S}_2\text{O}_7$ , (i)  $\text{KHSO}_4$ .
21. Name three outstanding chemical properties of concentrated sulfuric acid.
22. Name four uses of sulfuric acid.
23. Write equations for the preparation of sulfuric acid, starting with sulfur and continuing through the contact process.

### PROBLEMS

1. The density of sulfur vapor at  $444.6^{\circ}\text{C}$  is  $3.65\text{ g/L}$  at 1 atmosphere pressure. Show that most of the sulfur vapor at that temperature is in the form of  $\text{S}_8$  molecules. Assume that all molecules are either  $\text{S}_2$ ,  $\text{S}_4$  or  $\text{S}_8$ .
2. Calculate the molecular weight of sulfur vapor at  $1000^{\circ}\text{C}$  and 1 atmosphere. The density at those conditions is  $0.614\text{ g/L}$ .

3. A perfect cube of rhombic sulfur, 5 cm on an edge, is burned to sulfur dioxide and then converted by the contact process to sulfuric acid. How many g of concentrated sulfuric acid solution can be prepared?
4. How many liters of oxygen at 700 mm and 25°C are required to burn 50 g of sulfur to sulfur dioxide.
5. How many g of sulfur may be formed by reaction of 50 liters of  $\text{SO}_2$  and 50 liters of  $\text{H}_2\text{S}$ , both at STP?



## CHAPTER 19



# ELECTRICAL ENERGY FROM CHEMICALS

Certain spontaneous chemical reactions may be harnessed in such a way that part of the energy normally converted to heat is converted to electrical energy. The conversion of chemical energy to electrical energy occurs in the lead storage battery of an automobile and in a flashlight battery.

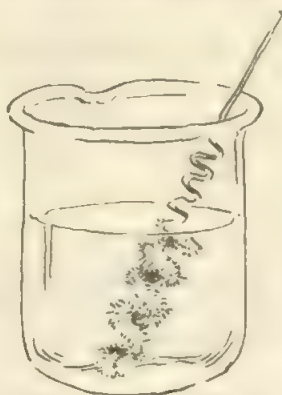
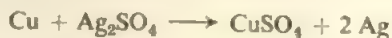


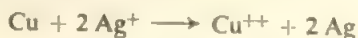
Figure 19.1. Metallic silver precipitated on a copper wire from silver sulfate solution.

Similar spontaneous reactions are also observed in a general chemistry laboratory. Among these is the reaction between copper metal and a silver salt solution. When a copper wire is placed in a silver sulfate solution (Fig. 19.1), it immediately turns silver. Within moments a silver "fur" covers the wire and, in time, may grow until the tiny silver branches are more than a half inch long. When the silver is rubbed from the copper wire, it is seen to be thin and rough. During the process the colorless silver sulfate solution has

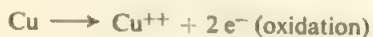
turned blue. Chemical analyses show that the solution contains cupric sulfate. Silver has left the solution; copper has entered in its place. The over-all equation is:



The net ionic equation is:



Sulfate ions remain in solution. This is an oxidation reduction equation; the half-cell reactions are:



and



The reaction consists in the transfer of electrons from copper atoms to silver ions. The copper atoms become ions and the silver ions become atoms. There are many other reactions in which metals replace less active metals in solution. Zinc metal dissolves in cupric sulfate solution to precipitate copper, as do iron and nickel. The reaction of zinc with strong acid solutions to produce hydrogen gas is a similar reaction.

## 1. PRIMARY CELLS

It might appear that electrons are exchanged from ion to atom when silver deposits on copper, that silver ions collide with copper atoms on the surface,

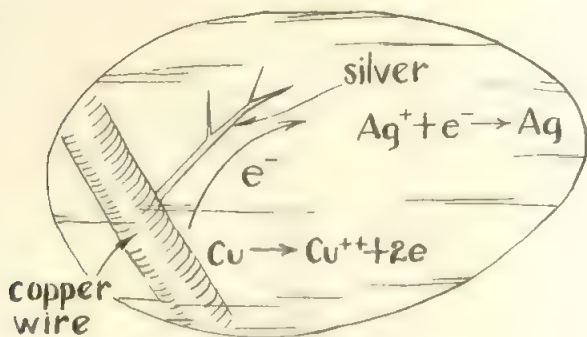
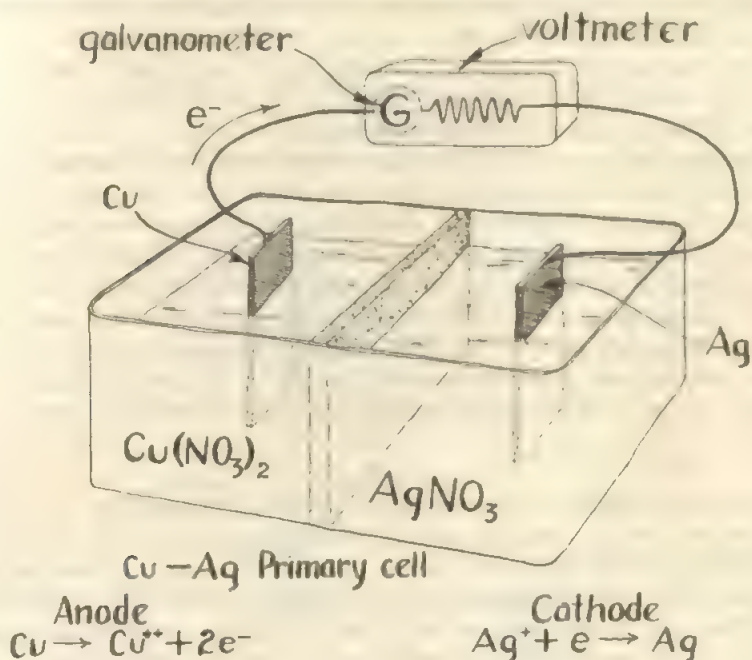


Figure 19.2. Metallic silver crystal on a copper wire.

and while in contact the electrons are transferred. This happens at first, until a layer of silver atoms covers the copper surface. However, silver atoms can precipitate on one another, growing out from the wire in branches (Fig. 19.2). When a silver atom adds to the end of a branch that is but a fraction of an inch long, it is precipitating at a distance of perhaps 1,000,000 atoms from the nearest copper atom. But silver metal is an excellent conductor of electricity. Electrons travel from the dissolving copper atom through the silver branch to be accepted by two silver ions at the silver surface.

A primary cell may be constructed by separating the dissolving and precipitating sites by a greater distance and connecting them by a metallic conductor above the solution (Fig. 19.3). In this cell the copper metal and the silver salt solution are not allowed to come in contact, but are in separate compartments divided by a porous plate. In one compartment a copper bar is suspended in a solution of cupric nitrate. A silver bar rests in a silver nitrate solution in the second compartment. The porous divider allows the solutions to come into contact, but it retards their mixing.



**Figure 19.3.** Silver being plated from an electrolytic cell.

When the two metal bars are connected by an electrical conductor through a galvanometer, the galvanometer needle is deflected; an electrical current is flowing. The electron stream flows from the copper bar to the silver. At the same time, the copper bar dissolves, the silver bar thickens and the copper nitrate solution becomes a deeper blue. It is clear that the same reaction is occurring that occurred when the copper wire was placed in the solution of copper sulfate. The overall reaction is the same:

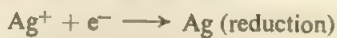


with the half-cell reactions taking place in different halves of the apparatus.

This apparatus is called a primary electrical cell. The copper and silver bars are called electrodes. Oxidation occurs at the copper electrode, which is called the *anode*:



Reduction occurs at the silver electrode, which is called the *cathode*:



The cell is a primary cell because it operates spontaneously. A secondary cell, an electrolysis cell, requires another cell or another source of electricity.

## 2. THE SOURCE OF ELECTROMOTIVE FORCE

When electrons flow from one point to another they are moved by electromotive force. Electromotive force consists in a difference in electric charge between two points. The greater the difference in electric charge, the greater the force with which electrons are drawn to the more positive of the two points. The volt is a unit of electromotive force.

Electrons flow from the copper anode to the silver cathode, therefore there is an electromotive force between them. To understand this, one must first analyze the situation existing at the surface of each electrode before the external conductor, the wire, is connected between them. Copper atoms have a slight tendency to lose the two valence electrons and to enter the solution as ions; a small proportion of the surface atoms do this. At the same time cupric ions collide with the electrode surface to gain electrons and remain. These two opposite reactions become equal and an equilibrium exists with respect to this reaction between the electrode surface and the solution:



A small concentration of electrons resides in the copper electrode, the magnitude of the charge depending upon the relative electronegativity of copper, the energy of hydration of the cupric ions and the bonding forces within copper metal. A like situation exists at the silver electrode. Atoms leave at a very slow rate, leaving their electrons behind, and ions return to the surface to take up electrons. This equilibrium exists at the electrode surface:



However, silver is more electronegative than copper and holds its valence electron more tightly than the copper atom holds its electrons. Therefore, the electron concentration at the silver electrode is less than at the copper. There exists a difference between the charges on the two electrodes. When the two are connected with a material that allows a free passage of electrons, the electrons flow from the region of greater concentration (the copper electrode) to the region of lower concentration (the silver electrode).

Unless the two electrode solutions come in contact, no current flows. The excess of positive cupric ions about the copper electrode would attract the excess electrons to the copper surface, and the leftover nitrate ions about the silver electrode would soon repel electrons at that point. The porous plate allows nitrate ions to pass from the silver compartment to the anode compartment to pair with the cupric ions coming into the solution. It also allows the cupric ions to migrate into the cathode compartment.



One can see from the two equilibria existing at the electrodes before connecting them together that the concentration of the two ions in their respective solutions affects the magnitude of the electron charge on the electrodes before the circuit is closed, and therefore the voltage of the cell. The higher the cupric ion concentration, the lower the electron concentration at the anode, and the lower the voltage. The greater the silver ion concentration, the lower the electron concentration at the cathode, and the greater the cell voltage. Unless otherwise stated, the concentration of all ions involved in the equilibria at the electrodes will be understood to be 1 molar.

### 3. CELL POTENTIALS (VOLTAGES)

Two simply constructed primary cells are sketched in Figure 19.4, the Daniell cell and the copper-silver cell discussed in the previous sections.

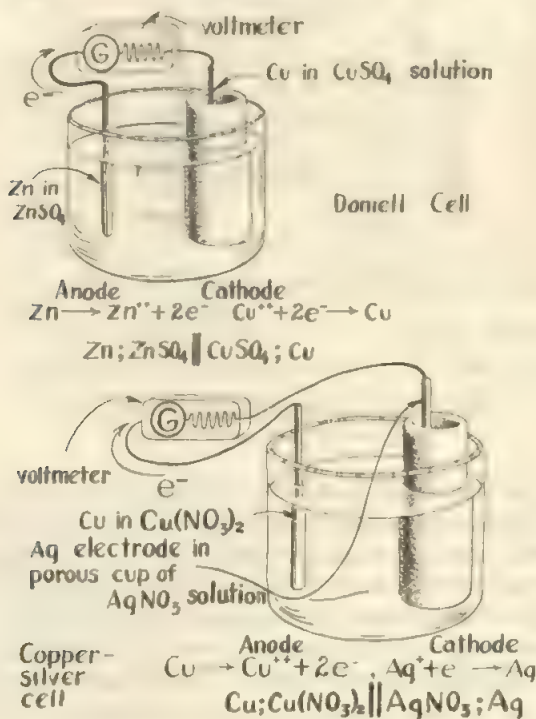


Figure 19.4. Two primary cells.

The walls of the porous cup replace the porous plate. The electrode reactions are those represented beneath the sketches, with oxidation occurring at the anode, and reduction at the cathode. Electrons move from left to right in the external conductor of both cells as sketched. During operation, zinc dissolves and copper plates (precipitates) in the Daniell cell, while copper dissolves and silver precipitates in the copper-silver cell.

The voltage of the Daniell cell is 1.10 volts, as compared to a voltage of 0.46 volts for the copper-silver cell. This is true only when the concentrations of the ions involved in the net ionic equations of the cell reactions are 1 molar. No attempt will be made to define voltage in fundamental terms. It suffices to say that if a set resistance wire is connected in series with a galvanometer across the electrodes of each cell (Fig. 19.4), the current will be  $1.10/0.46$  as great from the Daniell cell. A voltmeter is a high resistance connected in series with a galvanometer. It should be obvious that if one primary cell

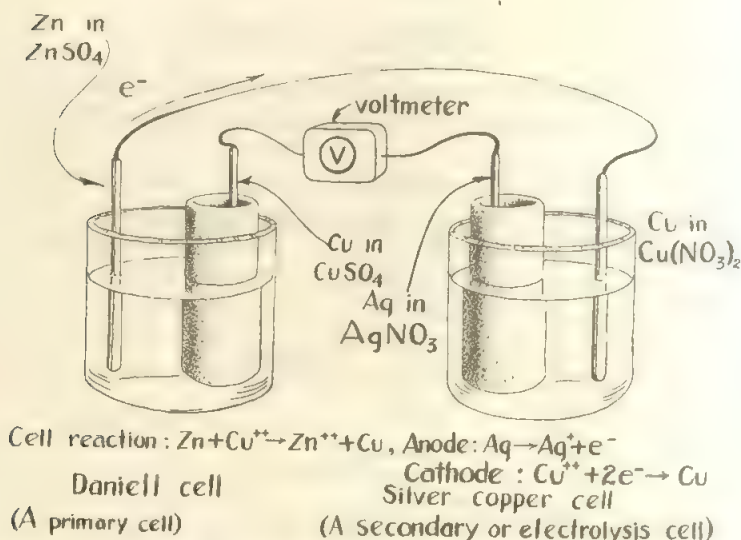


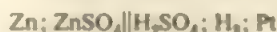
Figure 19.5. A primary and a secondary cell.

sends a current of more than double the amperage through a resistance that another does, it has a potential or voltage more than twice as great.

An interesting experiment may be performed to demonstrate that the Daniell cell has a greater electromotive force than the copper-silver cell. One can connect the two anodes and the two cathodes together (Fig. 19.5). When this is done the reactions in the Daniell cell are the same as before, but they are reversed in the copper-silver cell. Silver dissolves and copper precipitates. The latter cell has become a secondary cell or an electrolysis cell. Its motivation comes from the cell of higher voltage. The preparation of chlorine gas, sodium hydroxide solution, sodium metal, aluminum, copper and many other chemicals takes place in secondary cells where the electrons move as forced by an external electromotive force. The silver electrode, which was the cathode when the cell acted as a primary cell, is now the anode, because oxidation is occurring there. The copper electrode, formerly the anode, has become the cathode, because reduction of cupric ions occurs there. However, the polarity, now determined by the Daniell cell, is the same as before. The voltmeter in the circuit reads  $1.10 - 0.46 = 0.64$  volts.

## 4. TABLE OF ELECTRODE POTENTIALS (VOLTAGES)

In the cells discussed, a metal was either dissolved or precipitated at each electrode. Very often this is not the case. The cell represented by this notation:



is sketched in Figure 19.6. This cell contains the zinc electrode of the Daniell cell and the so-called hydrogen electrode. The hydrogen electrode consists of a platinum strip immersed in a solution of hydronium ions over which hydrogen gas is bubbled. The platinum metal provides a surface where hydrogen gas and hydronium ions may come, the hydrogen to give up electrons when the electrode acts as an anode, the hydronium ions to gain electrons

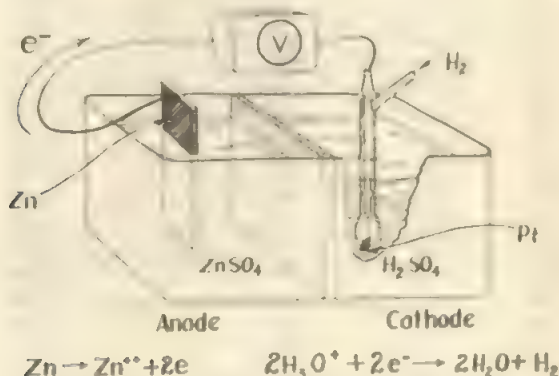


Figure 19.6. A zinc-hydrogen cell.

when the electrode is the cathode. The platinum also serves as a conductor to carry the electrons to or from the reaction site, as the case may be. Platinum is an inert metal and takes no other part in the reaction. When the zinc ion concentration and the hydronium ion concentration are both 1 molar and the hydrogen gas pressure is 1 atmosphere, zinc acts as the anode. Dissolving zinc liberates electrons which travel through the external conductor to the hydrogen cathode where they are absorbed in the reduction of hydronium ions, as shown by the electrode equations in Figure 19.6. The voltage of this cell is 0.76.

A primary cell may be made of a copper electrode and the hydrogen electrode (Fig. 19.7). The hydrogen electrode is the anode in this cell. Oxidation of hydrogen and the plating of copper occur as represented by the half-cell reactions. Electrons move from the hydrogen electrode to the copper electrode with a measured voltage of 0.34. The copper electrode is, therefore, 0.34 volts more positive than the hydrogen electrode. The hydrogen electrode is 0.76 volts more positive than the zinc electrode. The copper electrode should be  $0.76 + 0.34 = 1.10$  volts more positive than the zinc

electrode. This is true because the Daniell cell joins these two electrodes and has a voltage of 1.10. In the silver-copper cell, electrons flow to the silver electrode with a voltage of 0.46. The silver electrode should be  $0.34 + 0.46 = 0.80$  volts more positive than the hydrogen electrode. The hydrogen-silver cell has a potential of 0.80 volts.

Table 19.1. Electromotive Series

<i>Reductant</i>	<i>Oxidant</i>	<i>Voltage</i>
Cs	Cs <sup>+</sup>	-3.02
Li	Li <sup>+</sup>	-3.02
Rb	Rb <sup>+</sup>	-2.99
K	K <sup>+</sup>	-2.92
Ba	Ba <sup>++</sup>	-2.90
Sr	Sr <sup>++</sup>	-2.89
Ca	Ca <sup>++</sup>	-2.87
Na	Na <sup>+</sup>	-2.71
Mg	Mg <sup>++</sup>	-2.34
Be	Be <sup>++</sup>	-1.70
Al	Al <sup>+++</sup>	-1.67
Mn	Mn <sup>++</sup>	-1.05
Zn	Zn <sup>++</sup>	-0.76
Cr	Cr <sup>++</sup>	-0.71
S=	S	-0.51
Fe	Fe <sup>++</sup>	-0.44
Cd	Cd <sup>++</sup>	-0.40
Co	Co <sup>++</sup>	-0.28
Ni	Ni <sup>++</sup>	-0.25
Sn	Sn <sup>++</sup>	-0.14
Pb	Pb <sup>++</sup>	-0.13
H <sub>2</sub> , H <sub>2</sub> O	H <sub>3</sub> O <sup>+</sup>	0.00
Bi	Bi <sup>+++</sup>	+0.20
As	As <sup>+++</sup>	+0.30
Cu	Cu <sup>++</sup>	+0.34
I <sup>-</sup>	I <sub>2</sub>	+0.53
Fe <sup>++</sup>	Fe <sup>+++</sup>	+0.75
Hg	Hg <sub>2</sub> <sup>++</sup>	+0.80
Ag	Ag <sup>+</sup>	+0.80
Br <sup>-</sup>	Br <sub>2</sub>	+1.06
Cl <sup>-</sup>	Cl <sub>2</sub>	+1.36
Au	Au <sup>+</sup>	+1.68
F <sup>-</sup>	F <sub>2</sub>	+2.85

When one knows the voltages of the two cells with a common electrode and knows the anode in each case, he can calculate the voltage of the cell composed of the two dissimilar electrodes, as was done above.

The activity series, or electromotive series (Table 19.1), lists for each electrode the voltage of a cell joining that electrode and the hydrogen electrode, with the sign being *negative* if the hydrogen electrode is the cathode,



and *positive* if the hydrogen electrode is the anode. To find the voltage of a cell composed of two electrodes listed, subtract the more negative value from the more positive. The cathode will be the electrode with the more positive voltage in the table. Electrons will flow toward the electrode with the more positive number. For example, a cell of this notation:  $\text{Pb}; \text{Pb}(\text{NO}_3)_2 \mid \text{AgNO}_3; \text{Ag}$  has a voltage of  $0.080 - (-0.13) = 0.93$  volts. A cell with this notation:  $\text{Zn}; \text{Zn}(\text{NO}_3)_2 \mid \text{Pb}(\text{NO}_3)_2; \text{Pb}$  has a voltage of  $-0.13 - (-0.76) = 0.63$  volts; zinc is the anode. These voltages are obtained only when the ionic concentration is 1 molar.

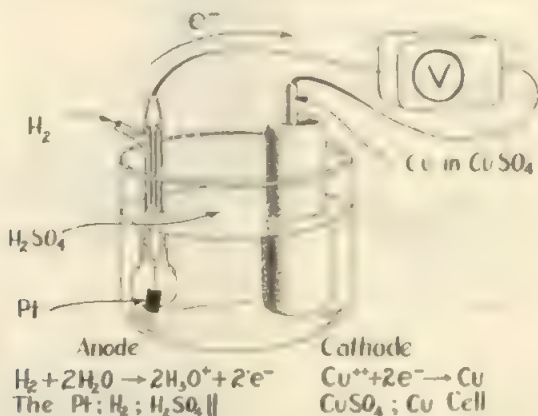


Figure 19.7. The copper-hydrogen cell.

## 5. SOME COMMON PRIMARY CELLS

### A. THE GRAVITY CELL

The primary cell that provided electricity for the old transcontinental telegraph was the gravity cell (Fig. 19.8a), a variation of the Daniell cell. This cell is interesting because an ingenious arrangement makes it unnecessary to divide it into two compartments. The copper electrode, in the form of a "crowfoot," rests on the bottom of a cylindrical glass vessel, surrounded by a copper sulfate solution. At the top of the cell is a zinc crowfoot electrode in a solution containing zinc sulfate and sodium sulfate. Because the copper sulfate solution is more dense than the zinc sulfate-sodium sulfate solution, it tends to remain on the bottom under the influence of gravity. Hence the name gravity cell.

Operation of the cell tends to keep the copper ions down about the cathode. For this reason, when the cell is not in use, the electrodes are connected through a large resistance. A small but continuous current flows through the cell. When current is drawn from the cell, cupric ions leave the solution in the neighborhood of the cathode and are precipitated as atoms on the cathode. Sulfate ions remain behind and give a negative charge to the area surrounding

the copper (Fig. 19.8b). Cupric ions are attracted to the negative area and remain about the cathode. At the same time zinc ions enter the solution about the anode. The existence of more positive ions than negative ions about the anode gives the area a positive charge and the sulfate ions are attracted to the anode. Zinc ions tend to move from the more positive anode solution toward the cathode along with the cupric ions. This presents no difficulty,

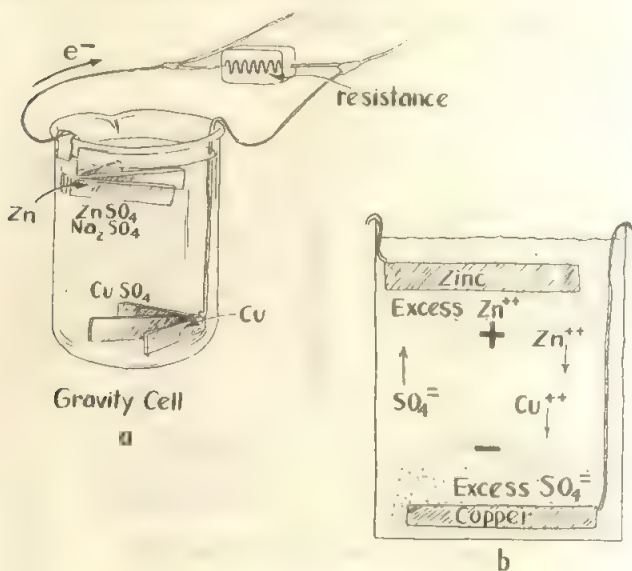
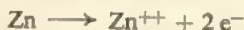


Figure 19.8. Daniell cell.

because zinc ions will not react with copper. One needs only to keep cupric ions from the zinc electrode.

### B. THE DRY CELL

The dry cell is the most familiar of all primary cells. Flashlight batteries are dry cells. The dry cell is not completely dry, but it contains a stiff paste of water, ammonium chloride, zinc chloride and manganese dioxide surrounding a graphite electrode, all enclosed in a zinc container (Fig. 19.9). At the inner surface of the zinc container this reaction occurs:

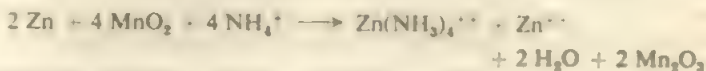


This is an oxidation reaction, and the zinc is the anode. The graphite rod serves as an inert electrode much as the platinum foil in the hydrogen electrode. At its surface, manganese dioxide and ammonium ions rearrange to new substances with the absorption of electrons:



The graphite rod is the cathode. Electrons flow from zinc to graphite through

an external conductor. Zinc ions form a complex ion with the ammonia formed ( $\text{Zn}(\text{NH}_3)_4^{++}$ ), so that no odor of ammonia is detectable. The overall reaction is:



The cell finally fails to produce electricity when either the ammonium

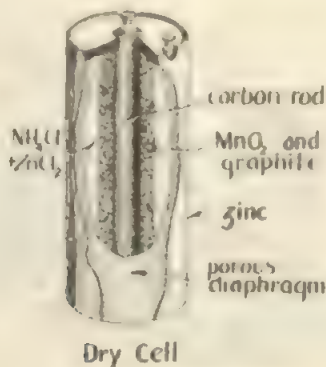


Figure 19.9. The dry cell.

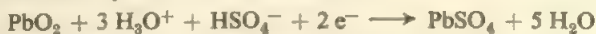
chloride or the manganese dioxide in the vicinity of the cathode is depleted or when the zinc container is eaten through and lets the liquid out. If it stands overnight, a dead cell may have a temporary revival. Some ammonium chloride solution may diffuse to the cathode. Important characteristics of dry cells are their lightness and the absence of either acid or bases in the fluid.

### C. THE LEAD STORAGE CELL

The source of electricity to start the automobile and to ignite the gasoline-air mixture in the cylinders is a battery of either three or six lead storage cells. The electrodes of a lead storage cell are quite similar. The anode is a lead grid with spongy lead pressed into the gridwork. The cathode is a lead grid with lead oxide in the grid (Fig. 19.10). The electrodes are suspended in a solution of sulfuric acid. The lead grids take no part in the cell reactions, but carry the current to the lead battery terminals. In operation spongy lead on the anode dissolves, but the lead ion formed precipitates with the sulfate present as lead sulfate on the plate:



Lead oxide dissolves at the cathode to become lead ions, which precipitate as lead sulfate in place of the oxide:



The overall reaction is:



Lead sulfate forms at both electrodes; sulfuric acid is consumed and water is formed. The cell is discharged when the spongy lead and lead oxide are almost completely converted to lead sulfate and when the sulfuric acid is reduced to a very low concentration. The sulfuric acid concentration is most easily checked. Sulfuric acid has a density about twice that of water. When the cell is discharged, the density of the solution approaches that of water. The density is tested with a hydrometer.

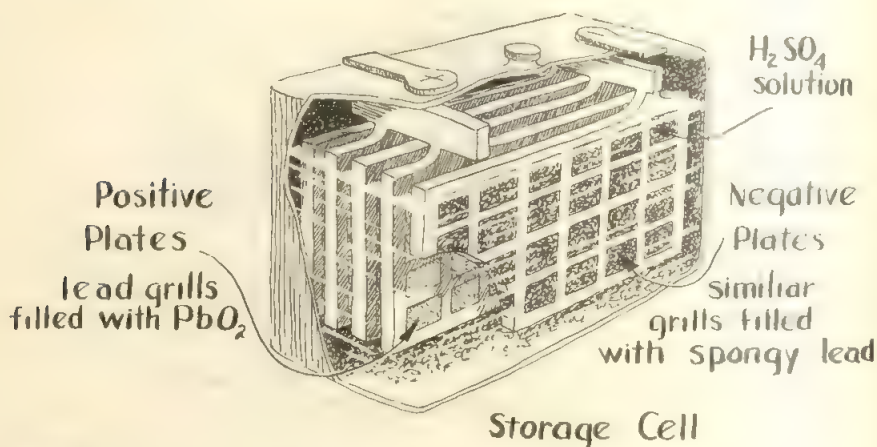


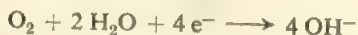
Figure 19.10. The lead storage cell.

But a lead storage cell can be recharged, that is, the lead oxide, the spongy lead and the sulfuric acid can be restored by reversing the flow of electrons. This is done constantly by the generator while the engine is operating. It impresses a higher voltage than the cell and changes it (during charging) to a secondary cell. The lead storage cell lives many lives.

Each cell has 2 volts. Three cells or 6 cells are connected anode to cathode to give either 6 or 12 volts. Each storage cell has a cathode and an anode of several plates. These larger electrodes are capable of greater power, a greater current at the same voltage, or of a longer life, for more reactants are present. Electrical energy depends upon both the voltage and the quantity of electricity that flows.

## 6. CORROSION

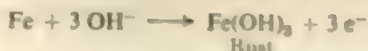
The corrosion (oxidation) of metals in the atmosphere is often related to the reactions that occur in primary cells. Consider a drop of water on an iron surface (Fig. 19.11). This constitutes an electrical cell. The edge of the drop on the iron surface is the cathode by the absorption of atmospheric oxygen:



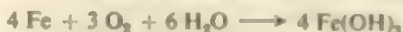
Hydroxide ions diffuse throughout the droplet. Electrons are conducted



away from the center of the drop, where the anode reaction occurs, by the iron:



The brown precipitate dries to ferric oxide. The overall balanced reaction is:



Iron is often coated with less active metals (such as tin) to prevent corrosion. Oxidation of tin is very slow and the iron is protected until the tin corrodes through or is broken in one spot. The tin then becomes a liability, because it offers a better surface for the reaction with oxygen than does iron. Iron oxidizes at the break more rapidly than if no tin were present.

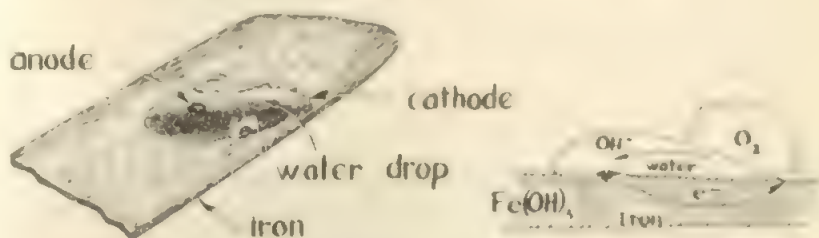


Figure 19.11. Corrosion.

Iron is often coated with zinc to protect it from atmospheric oxidation. Galvanized ware is zinc-coated iron. Zinc is more reactive than iron. It might appear that oxidation would be hastened. But the presence of zinc retards the oxidation of iron when a break occurs in the coating. When a drop of water covers the hole, more active zinc is dissolved in preference to iron. Often the zinc coating almost completely disappears before a hole penetrates the iron.

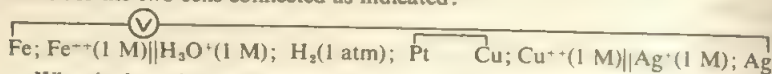
## EXERCISES

1. Name three metals that will replace silver in solution.
2. What is meant by a spontaneous reaction?
3. Write three oxidation-reduction reactions.
4. Write the half-cell equations for the dissolving of zinc in copper sulfate solution.
5. What charge does the anode bear in a primary cell?
6. Define anode. The definition should hold for both primary and secondary cells.
7. Write the overall reaction, the net ionic equation and the electrode reactions for the copper-silver cell, the zinc-hydrogen cell and the copper-hydrogen cell.
8. Describe how one might obtain the electrode voltage of the tin-tin ion electrode.
9. Could one use zinc in place of platinum for the hydrogen electrode? Explain.
10. What is the purpose of the porous plate?
11. Write the reactions occurring at the electrodes while the lead storage cell is being charged.

## PROBLEMS

1. a. Sketch this cell:  $\text{Mg}; \text{Mg}^{++}(1 \text{ M}) || \text{Ag}^+(1 \text{ M}); \text{Ag}$ .
- b. Identify anode and cathode.
- c. Indicate direction of electron flow.
- d. Calculate the voltage of the cell.

2. Consider the two cells connected as indicated:



- a. What is the voltage of the cell?
  - b. Indicate the direction of electron flow in both external conductors.
  - c. Write both oxidation half-cell equations.
  - d. Write both reduction half-cell equations.
  - e. What substances are dissolved? What substances are formed?
3. The cell:  $\text{Mg; Mg}^{2+}(1\text{ M}) \parallel \text{Ag}^+(1\text{ M}); \text{Ag}$  is allowed to discharge until the concentration of magnesium ion is increased to 1.25 M. What is the silver ion concentration? Has the voltage changed during the discharging? If so, has it increased or decreased?

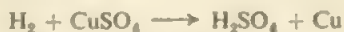
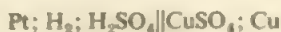
# CHAPTER 20

## OXIDATION AND REDUCTION

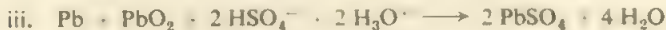
Many chemical reactions involve oxidation-reduction. All reactions occurring in cells discussed in the previous chapter are oxidation-reduction reactions. The reaction of the Daniell cell is oxidation-reduction:



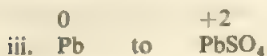
Oxidation-reduction occurs in the cell represented by:



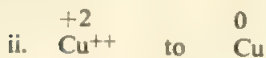
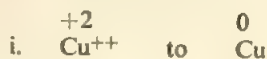
The reaction occurring in the lead storage cell is oxidation-reduction:



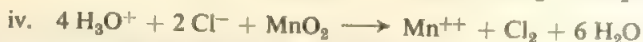
Oxidation has occurred, because in each reaction an element has increased in oxidation state:



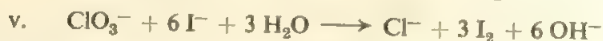
Reduction has occurred, because in each reaction an element has decreased in oxidation state:



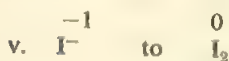
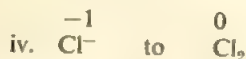
These reactions need not occur in electrical cells. When occurring in cells, one can gain energy from them. Reaction (i) occurs when a zinc wire is immersed in a copper sulfate solution. Some reactions that cannot occur in cells are also oxidation-reduction reactions. The reaction occurring when concentrated hydrochloric acid is heated with manganese dioxide to produce chlorine is oxidation-reduction:



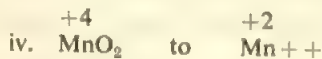
Oxidation-reduction occurs when a basic potassium chlorate solution is mixed with a solution of potassium iodide to release iodine.



An element undergoes an increase in oxidation state (is oxidized) in each of these reactions:



While another element in each reaction suffers a decrease in oxidation state (is reduced):



Notice that oxidation occurs simultaneously with reduction. This is always the case, because oxidation is a loss of electrons and reduction is a gain of electrons. The loss must equal the gain. Observe the electron loss and gain in the five equations discussed above (Table 20.1).

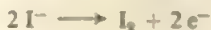
These equations showing oxidation or reduction are named half-cell equations, because they indicate reactions that occur or might occur at one electrode, or one-half the reaction of an electrolytic cell.



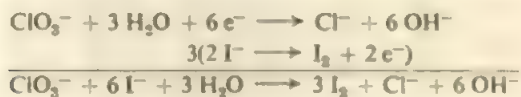
Notice further that the half-cell equations are combined together in such a way that there is no net gain nor loss in electrons. For example, in equation (v) 6 electrons are needed in the reduction:



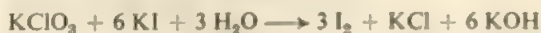
When iodide ions change to an iodine molecule, only 2 electrons are freed:



Therefore, 6 iodide ions must change to 3 iodine molecules while 1 chlorate ion changes to 1 chloride ion to give the 6 electrons needed:



This is the balanced net ionic equation. Were one to use the equation to determine the relative amounts of reagent potassium chlorate required to oxidize a given amount of potassium iodide, he would have to add the necessary spectator ions to the equation.



The substances, potassium chlorate and potassium iodide, are needed in the mole ratio of 1 to 6, respectively, to furnish the proper proportion of their negative ions.

### ION-ELECTRON METHOD OF BALANCING EQUATIONS

There are several different methods for balancing oxidation-reduction equations. The method just demonstrated is called the *ion-electron method*. Steps for this method will be summarized below. For the purpose of simplicity, the hydronium ion will be represented as  $\text{H}^+$  in this chapter. One must remember that each  $\text{H}^+$  is attached to a water molecule not shown. Should one desire to obtain the balanced equation with hydronium ions, he must change all  $\text{H}^+$  in the final equation to  $\text{H}_3\text{O}^+$  and then add an  $\text{H}_2\text{O}$  to the opposite side of the equation for every hydronium formed.

1. Write the equation in the net ionic form.
2. Separate the equation into two parts by pairing ions or compounds containing the same element in changed oxidation states.
3. Balance each part as follows:
  - A. In an acid solution:
    - (1) Balance the elements by using  $\text{H}_2\text{O}$  and  $\text{H}^+$  as needed.
    - (2) Balance electrically by adding electrons to get the half-cell equation.
  - B. In a basic solution:
    - (1) Balance the elements by adding  $\text{H}_2\text{O}$  and  $\text{OH}^-$  as needed.

Note:  $2 \text{OH}^- \rightarrow \text{H}_2\text{O}$ , O (an oxygen contained in a compound or ion)

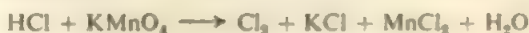
**Table 20.1. Half-Cell Equations Showing Gain and Loss of Electrons**

[illegible]

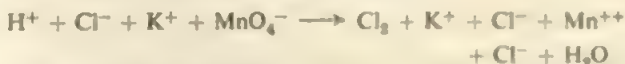
- (2) Balance electrically by adding electrons to get the half-cell equation.
4. Multiply the half-cell equations by appropriate factors so that the number of electrons is equal in each equation and then combine
  5. Reduce the coefficients of the equation to the lowest possible integers.

EXAMPLE 1. Potassium permanganate reacts with concentrated hydrochloric acid to produce chlorine gas and manganous ion.

Overall equation:



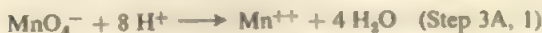
Complete ionic equation (writing  $\text{H}_3\text{O}^+$  as  $\text{H}^+$ ):



Net ionic equation (unbalanced):



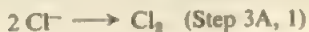
One half-cell reaction (Step 2):



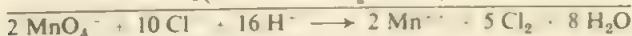
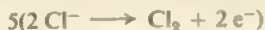
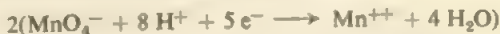
(Add  $\text{H}_2\text{O}$  to balance O's first, then add  $\text{H}^+$  to balance H's).



The other half-cell reaction (Step 2):



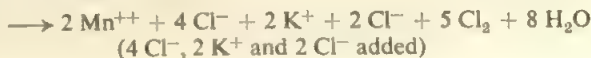
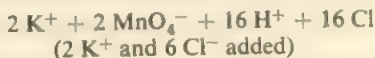
Combining half-cell reactions (Step 4):



Step 5 does not apply here.

Notice that all products and reactants, except the hydronium ion ( $\text{H}^+$ ) and water, must be known. These two are added as required in the balancing.

One can use the balanced equation (Step 4) to determine the mass of potassium permanganate that will react with a certain volume of dilute hydrochloric acid (6 M solution) only by "combining" ions together and adding the necessary spectator ions:



An equal number of each kind of ion was added to each side of the equation to give a balanced total ionic equation. The chemicals are required in the mole ratios shown in this equation:



2 moles of  $\text{KMnO}_4$  react with 16 moles of  $\text{HCl}$  to yield 5 moles of chlorine gas.

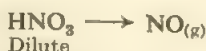
One may now determine that 25 g of  $\text{KMnO}_4$  will react with a calculated volume of dilute  $\text{HCl}$

$$\frac{25 \text{ g}}{158 \text{ g/mole}} \times \frac{16}{2} \times \frac{1}{6 \text{ moles/L}} \times 1000 \text{ ml/L} = 211 \text{ ml of dilute HCl}$$

to yield

$$\frac{25 \text{ g}}{158 \text{ g/mole}} \times \frac{5}{2} \times 22.4 \text{ L/mole} = 8.86 \text{ L of Cl}_2 \text{ at STP}$$

**EXAMPLE 2.** Balance the half-cell equation for the reduction of dilute nitric acid to nitric oxide in an acid solution:



In net ionic form:



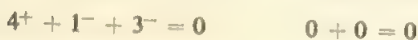
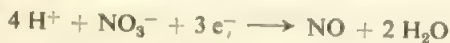
The hydronium ion is left out. This is all of the half-cell equation that is needed to begin balancing. The nitrate ion was used up; and nitric oxide gas formed. But  $\text{NO}_3^-$  cannot change to  $\text{NO}$ ; 2 oxygen atoms would be lost. The only possible product not accounted for is water.



Hydrogens are unbalanced. They must have come from the hydronium ions present.



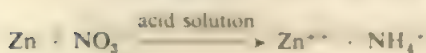
The equation is balanced elementally (that is, atoms balance) but not electrically. Each of 4 hydronium ions are minus 1 electron, and 1 nitrate ion has an extra electron, but the products are neutral. For 4  $\text{H}^+$  and 1  $\text{NO}_3^-$  to become 1  $\text{NO}$  and 2  $\text{H}_2\text{O}$ , 3 electrons must be absorbed:



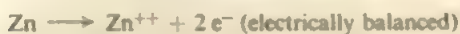
The half-cell equation is balanced. Electrons are gained by the reactants; reduction has occurred.

**EXAMPLE 3.** Zinc metal reacts with the nitrate ion in an acid solution to give the zinc ion and ammonium ion. Obtain the balanced net ionic equation:

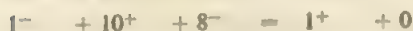
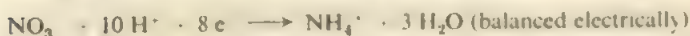
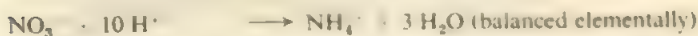
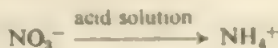




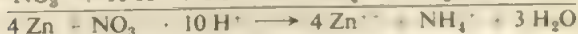
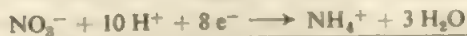
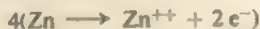
One half-cell equation (oxidation):



Reduction half-cell equation:



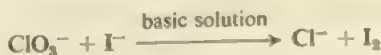
Adding equations together so that electrons drop out:



(balanced net ionic equation)

Equations of reactions occurring in basic solutions are not encountered so frequently, and the equations are more difficult to balance. One example will be discussed.

EXAMPLE 4. As stated before in this chapter, the chlorate ion in a basic solution oxidizes the iodide ion to  $\text{I}_2$ . The only other product is the chloride ion. Balance the equation:



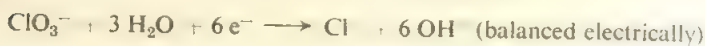
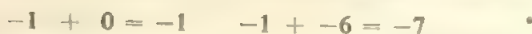
Choosing the simplest half-cell equation (oxidation):



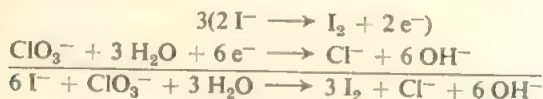
The reduction half-cell equation:



One must balance the elements in the equation by adding only water ( $\text{H}_2\text{O}$ ) and the hydroxide ion ( $\text{OH}^-$ ). To keep the hydrogen balanced, one must add 1  $\text{H}_2\text{O}$  to one side and 2  $\text{OH}^-$  to the other:



Combining half-cell equations:



### OXIDIZING AND REDUCING AGENTS

In the equation immediately above, the iodide ion lost electrons; iodine increased in oxidation state; the iodide ion was oxidized. How was it accomplished? By the chlorate ion and water in a basic solution. The chlorate ion and water in a basic solution are the *oxidizing agents*.

In the same equation, the chlorate ion and water gained electrons in becoming the chloride ion and the hydroxide ion; the oxidation state of chlorine decreased from +5 to -1; chlorate and water were reduced. The iodide ion gave the chlorate ion and water the electrons, and, therefore, the iodide ion is the *reducing agent*.

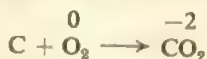
One can say that the iodide ion lost electrons. However, it is not correct to say that the chlorate ion gained electrons. The chlorate ion and water gained electrons to become hydroxide ions and chloride ions. The chlorate ion alone is not the oxidizing agent. Further, since a change in the concentration of any one of the ions or water changes the oxidizing strength, the chlorate, water, chloride and hydroxide ions together are the oxidizing agency.

### OTHER OXIDATION-REDUCTION EQUATIONS

Some so-called oxidation-reduction equations do not occur in water solution, do not involve ions, and cannot be balanced by the method here. One of these might well have been the first reaction called oxidation. One reaction of burning coal is:



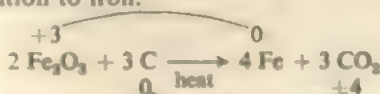
The oxidation state of carbon is raised from 0 to +4 as indicated. The oxidation state of oxygen is decreased from 0 to -2:



No electron change is obvious. Neutral carbon and an oxygen molecule with its shared electrons merely share together. Initially, it was thought that carbon dioxide was ionic, that oxide ions carried a charge of -2 and that electrons were exchanged in the reaction.

Reduction may well have been named by the reaction of coke at higher

temperature with an iron oxide ( $\text{Fe}_2\text{O}_3$ ) in an ore to reduce it in weight and composition to iron.



Again, although oxidation states change, no clear case of electron transfer is apparent.

Perhaps the method for balancing oxidation-reduction equations should be expanded to include this type of reaction. However, most reactions studied in elementary chemistry occur in water solutions and involve ions. Those that do not are generally easily balanced by inspection.

### EXERCISES—SET I

1. Define oxidation, reduction, oxidation state, oxidizing agent and reducing agent.
2. Write the oxidation states (numbers) of all elements in the following formulas: (a)  $\text{KCl}$ , (b)  $\text{KClO}_3$ , (c)  $\text{ClO}_4^-$ , (d)  $\text{BrO}$ , (e)  $\text{PO}_4^{3-}$ , (f)  $\text{HSO}_4^-$ , (g)  $\text{MnO}_2$ , (h)  $\text{S}_4\text{O}_6^{2-}$ , (i)  $\text{H}_2\text{SO}_4$ , (j)  $\text{Na}_2\text{S}_2\text{O}_3$ , (k)  $\text{Cr}_2\text{O}_7^{2-}$ .
3. In this balanced half-cell equation:



- a. What element changes oxidation state?
  - b. Is it oxidized or reduced?
  - c. What has gained electrons in this reaction?
4. Mercuric sulfide is dissolved in aqua regia (a mixture of concentrated  $\text{HCl}$  and  $\text{HNO}_3$ ) to form sulfur, the tetrachloromercurate(II) ion,  $\text{HgCl}_4^{2-}$ , and nitrogen dioxide gas,  $\text{NO}_2$ .
    - (a) Write a balanced net ionic equation.
    - (b) What is the oxidizing agent?
    - (c) What is oxidized?

### EXERCISES—SET II

Obtain the balanced net ionic equation for each of these equations by the ion-electron method.

1.  $\text{Cu}^{++} + \text{I}^- \longrightarrow \text{Cu}^+ + \text{I}_2$
2.  $\text{CeO}_2 + \text{I}^- \longrightarrow \text{Ce}^{+++} + \text{I}_2$  (in acid)
3.  $\text{Cu} + \text{H}^+ + \text{NO}_3^- \longrightarrow \text{Cu}^{++} + \text{NO} + \text{H}_2\text{O}$  (conc. acid)
4.  $\text{Cu} + \text{H}^+ + \text{NO}_3^- \longrightarrow \text{Cu}^{++} + \text{NO} + \text{H}_2\text{O}$  (dil. acid)
5.  $\text{Zn} + \text{H}^+ + \text{NO}_3^- \longrightarrow \text{Zn}^{++} + \text{NH}_4^+ + \text{H}_2\text{O}$  (dil. acid)
6.  $\text{C} + \text{NO}_3^- \longrightarrow \text{CO}_2 + \text{NO}_2 + \text{H}_2\text{O}$  (in acid)
7.  $\text{Sn} + \text{HNO}_3 \longrightarrow \text{SnO}_2 + \text{N}_2 + \text{H}_2\text{O}$  (dil. acid)
8.  $\text{Cr}_2\text{O}_7^{2-} + \text{Fe}^{++} + \text{H}^+ \longrightarrow \text{Fe}^{+++} + \text{Cr}^{+++} + \text{H}_2\text{O}$
9.  $\text{CrO}_4^{2-} + \text{I}^- + \text{H}^+ \longrightarrow \text{Cr}^{+++} + \text{I}_2 + \text{H}_2\text{O}$
10.  $\text{S} + \text{H}^+ + \text{HSO}_4^- \longrightarrow \text{SO}_2 + \text{H}_2\text{O}$
11.  $\text{Co}^{++} + \text{I}^- + \text{IO}_3^- + \text{H}_2\text{O} \longrightarrow \text{Co}(\text{OH})_2 + \text{I}_2$
12.  $\text{Sb}^{+++} + \text{MnO}_4^- \longrightarrow \text{H}_3\text{SbO}_4 + \text{Mn}^{++}$  (in acid)

13.  $\text{I}^- + \text{MnO}_4^- \longrightarrow \text{I}_2 + \text{Mn}^{++}$  (in acid)
14.  $\text{H}_2\text{S} + \text{H}^+ + \text{NO}_3^- \longrightarrow \text{S} + \text{NO}$
15.  $\text{NH}_3 + \text{O}_3 \longrightarrow \text{NO} + \text{H}_2\text{O}$
16.  $\text{MnO}_2 + \text{C}_2\text{O}_4^{2-} + \text{H}^+ \longrightarrow \text{Mn}^{++} + \text{CO}_2$
17.  $\text{MnO}_4^- + \text{AsO}_3^{3-} \longrightarrow \text{MnO}_2 + \text{AsO}_4^{3-} + \text{OH}^-$
18.  $\text{CaOCl}_2 + \text{I}^- \longrightarrow \text{I}_2 + \text{Ca}^{++} + \text{Cl}^-$  (in acid)
19.  $\text{Mn}^{++} + \text{S}_2\text{O}_8^{2-} \longrightarrow \text{MnO}_2 + \text{HSO}_4^- + \text{H}^+$
20.  $\text{TeO}_3^{2-} + \text{I}^- \longrightarrow \text{Te} + \text{I}_2$  (in acid)
21.  $\text{U}^{++} + \text{MnO}_4^- \longrightarrow \text{Mn}^{++} + \text{UO}_2^{++}$  (in acid)
22.  $\text{As} + \text{H}^+ + \text{NO}_3^- \longrightarrow \text{H}_3\text{AsO}_4 + \text{NO}$
23.  $\text{ClO}_3^- \longrightarrow \text{ClO}_4^- + \text{ClO}_2$
24.  $\text{Pd} + \text{HSO}_4^- \longrightarrow \text{Pd}^{++} + \text{SO}_2$

### PROBLEMS

1. How many liters of  $\text{NO}_2$  at STP are formed by the reaction of 24.0 g of copper metal with an excess of concentrated nitric acid?
2. How many grams of potassium dichromate,  $\text{K}_2\text{Cr}_2\text{O}_7$ , react to oxidize 100 ml of 2.0 M  $\text{Fe}^{++}$  to ferric ion?
3. How many grams of  $\text{MnO}_2$  are required to produce 2.60 mole of electrons when reduced to manganous ion in an acid solution?
4. How many ml of hot concentrated nitric acid (15 M) react to dissolve a dime? A dime weighs 2.50 g and is 90% silver and 10% copper.



## CHAPTER 21

# NITROGEN AND PHOSPHORUS

[illegible]

Nitrogen and phosphorus are the first and second members of Group V in the Periodic Table. A consideration of some of the physical properties (Table 21.1) shows that the trend is as expected for the group.

Table 21.1. Some Physical Properties of Elements of Group V

	<i>Nitrogen</i>	<i>Phosphorus</i>	<i>Arsenic</i>	<i>Antimony</i>	<i>Bismuth</i>
Melting Point °C	210.0	44.1	814.5	630.0	271.0
Boiling Point °C	-195.8	280.5	610 (sublimes)	1380.0	1450.0
Density of solid g/cm <sup>3</sup>	0.879	1.82	5.7	6.6	9.8

Nitrogen, the first element, is the only gas; the rest are solids. The densities, as well as the molecular weights, of the solids increase from nitrogen to bismuth.

In chemical properties, there is a great variation. All have 5 electrons in the valence shell. The possible oxidation states vary from  $-3$  to  $+5$ . However, because of the diagonal relationship of increasing electronegativity (up and to the right) nitrogen and phosphorus are definitely non-metals, seeking an ionic charge of  $-3$  or sharing with other non-metals, whereas bismuth is a metal forming most of its compounds by loss of three valence electrons. Arsenic and antimony lie in between, possessing some metallic and some non-metallic properties. The change from non-metallic to metallic properties is reflected in the melting points which decrease again from arsenic through antimony, to bismuth.

## 1. NITROGEN AND WHITE PHOSPHORUS

A. *Phosphorus* is an active chemical with the following properties:

- (1) It is never found free in nature, but always occurs as a phosphate.
  - (2) Waxy white phosphorus quickly turns yellow in air.
  - (3) Sticks of phosphorus fume in air as oxidation occurs on their surface. If it is finely divided, phosphorus bursts into flames when it comes in contact with air.\* As a safety measure, white phosphorus is stored under water.
  - (4) Flammable material that comes in contact with phosphorus bursts into flames.†
  - (5) White phosphorus is a deadly poison. It attacks the bones in the jaw and nose and causes them to crumble. Skin burns from phosphorus are painful and heal very slowly. Phosphorus is often used in rat poisons. The vapors of phosphorus are also deadly.
  - (6) White phosphorus is soluble in organic solvents, especially in carbon disulfide.‡
- B. *Nitrogen*, on the other hand, is a relatively inactive gas. It occurs free in nature. Eighty per cent of dry air is nitrogen gas. Thus many reactions involving chemicals that decompose in air are carried out in the presence of nitrogen. Nitrogen is obviously not poisonous.

An apparent contradiction of the inactivity of nitrogen is the fact that it occurs in a great multitude of compounds. When it is not in its elemental state, nitrogen is changed readily from one compound to another. Further,

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\* Because of this property, phosphorus was used as an incendiary during World War II. It is difficult to extinguish the flames from phosphorus with water, because they burn again when the sun dries the phosphorus. Phosphorus is also used in tracer bullets to light their paths.

† The "will-o'-the-wisp," an eerie gas flame appearing over marshy land, is burning methane gas ignited by traces of white phosphorus.

‡ An interesting but tricky demonstration is carried out by painting a picture on paper with a solution of white phosphorus in carbon disulfide. When the volatile carbon disulfide evaporates, the picture is etched in flame.

nitrogen contributes properties to its compounds similar to those contributed by other active non-metals.

## 2. STRUCTURES OF NITROGEN AND PHOSPHORUS

The difference in chemical reactivity seems to be due to the difference in molecular structure of the two elements. Nitrogen gas has a density that corresponds to diatomic molecules ( $N_2$ ) and has the electronic structure shown in Figure 21.1a.

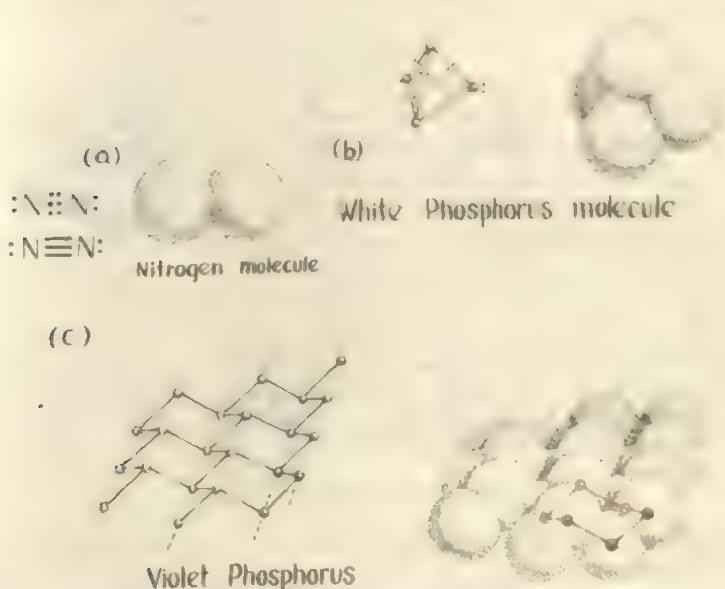


Figure 21.1. Molecular structures of nitrogen gas, white and violet phosphorus.

The two nitrogen atoms are bonded together with a triple bond, 6 shared electrons. The formula of phosphorus vapor is  $P_4$ . The molecular weight of phosphorus vapor by density calculations is 124. Electron diffraction studies have shown the four phosphorus atoms to be arranged at the corners of a regular tetrahedron. If so, single bonds, one shared pair of electrons, bind each atom to each of the other three in the molecule (Fig. 21.1b). The group of 4 atoms in the molecule resembles a stack of 4 cannonballs, as sometimes seen on a courthouse square. Studies indicate that the same  $P_4$  molecules are packed tightly together in white phosphorus.

When nitrogen combines with oxygen to give nitric oxide:



the stable triple bond in the nitrogen molecules must be broken. In the burning of white phosphorus, one single bond can be broken at a time;  $P_4O_6$  is the first product of the combustion of phosphorus. In  $P_4O_6$ , an

oxygen atom is "sandwiched" in between each pair of phosphorus atoms (Fig. 21.2b). The further oxidation product of burning phosphorus is  $P_4O_{10}$ , called phosphoric acid anhydride. The 4 additional oxygen atoms added above  $P_4O_6$  are merely added by coordinate bond formation to the phosphorus atoms at the corners.

Further confirmation that the reversal in reactivity of nitrogen and phosphorus is due to molecular structure is found in the existence of another and more stable form of phosphorus. White phosphorus is formed when the vapor is collected under water. When warmed, especially with a trace of iodine

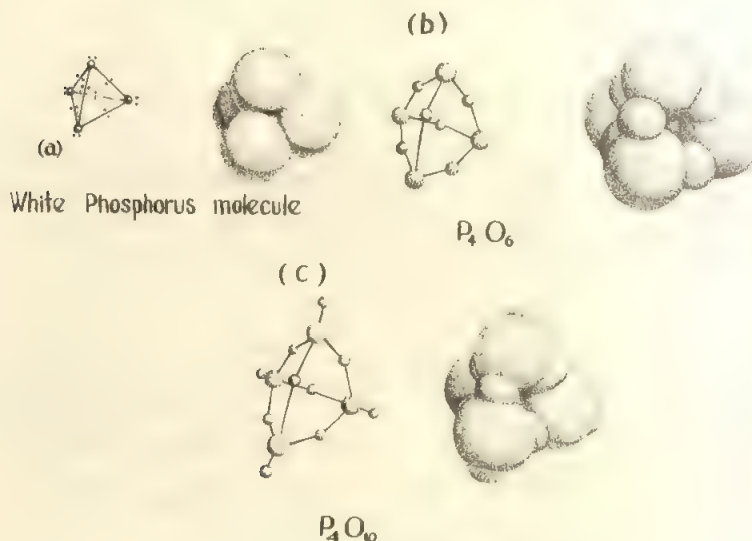


Figure 21.2. Oxides of phosphorus.

catalyst, white phosphorus is converted to red phosphorus, a form of violet phosphorus.

Violet, or red, phosphorus differs greatly from white phosphorus in other properties besides color:

- Violet phosphorus is much less active chemically. It will not burn in air unless heated above  $200^{\circ}\text{C}$ .
- It is non-poisonous.
- It is insoluble in almost all solvents. It will not dissolve in carbon disulfide.
- It neither melts nor boils at 1 atmosphere pressure, but it sublimes at  $416^{\circ}\text{C}$ , a temperature considerably above the melting and boiling points of white phosphorus. The melting and boiling points recorded in Table 21.1 are for white phosphorus.

The probable structure of violet phosphorus is illustrated in Figure 21.1c. The phosphorus atoms are continuous rings of 6 with alternate atoms being



raised above the plane. Each atom is bonded by a single shared pair of electrons to three more atoms. "Crinkled" sheets of atoms lay one above the other in a crystal of violet phosphorus. It is obvious that  $P_4$  molecules would be more easily separated from one another than would groups of atoms from a covalently bonded layer. Hence the lower melting and boiling points and the greater solubility of white phosphorus. One can see why the atoms in the layers would be less easily attacked by chemical agents.

In the allotropy of sulfur, the difference in rhombic and monoclinic sulfur was merely a difference in the pattern of packing the 8-atom molecule. Correspondingly small differences in properties were noted. A difference in molecular structure, as exists between white and violet phosphorus, is accompanied by a great change in properties.

Arsenic and antimony generally occur in brittle gray crystals resembling violet phosphorus in both structure and chemical activity. However, yellow, unstable, active, tetra-atomic forms of both are known. Bismuth on the other hand, exists primarily in a black, crystalline, metallic form.

When an electric discharge passes through nitrogen at low pressure (less than 1 mm) some change takes place that increases its reactivity. The nature of this *active nitrogen* is not understood, but it is assumed that nitrogen atoms separated by electrical energy are contained among the molecules. After the electric arc is turned off, an orange-colored glow may be seen, under best conditions, for nearly two hours. The glow is thought to be due to emission of energy as the atoms reunite. Many metals which will not react with ordinary nitrogen react with active nitrogen to produce nitrides:  $Ca_3N_2$ ,  $Zn_3N_2$  and  $Cu_3N_2$ .

### 3. OCCURRENCE

The elements of Group V are rather well known despite the fact that only phosphorus is abundant in nature; it comprises 0.118% of the earth's crust, as compared with a percentage of 0.0046 for nitrogen. All are known because they are readily accessible and their compounds are fairly easily separated and reduced to the element. Phosphorus occurs in concentrated phosphate deposits. Nitrogen is the major component of the mixture air (Table 21.2).

**Table 21.2. Approximate Percentage Composition of Dry Air**

Nitrogen	78.09	Neon	} .001
Oxygen	20.95	Helium	
Argon	0.93	Krypton	
Carbon dioxide	0.03		

Nitrogen is an indispensable element of the biosphere, the shell of living material around the earth. All living matter contains nitrogen in many

complicated compounds, and all living matter requires nitrogen compounds in its food. Much work in agriculture is concerned with supplying these nitrogen-bearing foods.

Nitrogen presents a paradox of "plenty in the midst of poverty." Despite the fact that nitrogen is not an abundant element, there are about 20 million tons of it in the air above each square mile of the earth's surface, far more than

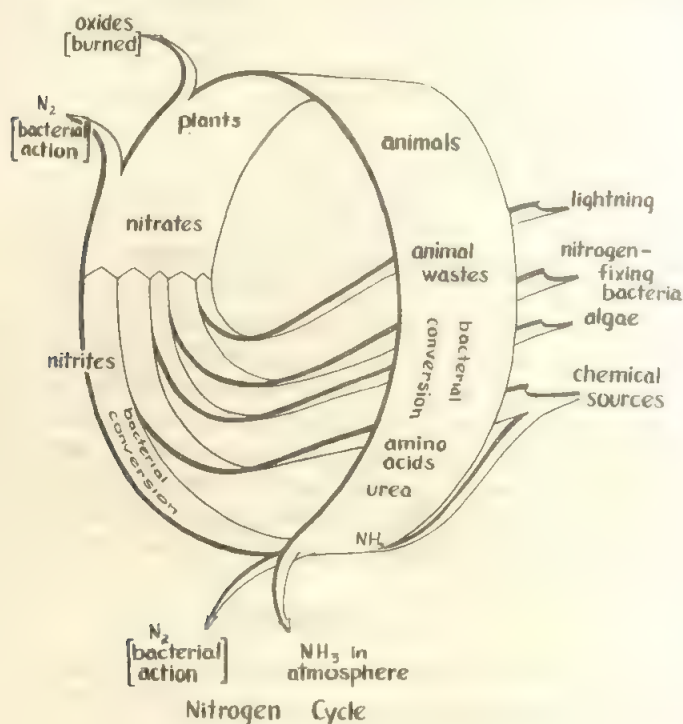


Figure 21.3. The nitrogen cycle.

enough to supply the nitrogen needed. But as mentioned before, nitrogen is inert and is reluctant to combine with other elements to form ions that dissolve in water for plant food. We are fortunate that nitrogen is not more reactive; if it were, all the oxygen in the air would combine with nitrogen.

Because of the difficulty in gaining nitrogen compounds nature passes its combined nitrogen from one living form to another in a complicated cycle (Fig. 21.3). Nitrogen is absorbed as nitrates and ammonium salts into plant roots. In the plants, the nitrogen is incorporated into amino acids and proteins. Animals eating the plants gain the proteins for themselves. As one animal eats another, nitrogen-containing proteins are distributed throughout the animal kingdom. Dead and decaying plant and animal tissues and wastes are decomposed by bacteria to ammonia, amino acids and urea, which in turn are decomposed to nitrites, then to nitrates, which are absorbed by plants to begin the cycle again. But the cycle is inefficient. Much

of the ammonia from decaying proteins is lost to the atmosphere. Certain bacteria convert the nitrogen in amino acids to nitrogen gas, which also is lost to the atmosphere. Plant wastes are burned and animal wastes are accumulated in areas where they are not needed.

The cycle is depleted to a much greater extent in farming areas than in wild uninhabited areas, because nitrogen is absorbed by the crops.

A process called nitrogen fixation supplements the cycle. Nitrogen fixation may occur in nature in three ways:

- A. Certain parasitic bacteria that grow on the roots of legume plants can absorb nitrogen from the air and combine it chemically for their own use. Furthermore, they store up more of the "fixed" nitrogen than they need and thus build up the nitrogen content of the soil.
- B. Certain microscopic plants, called algae, which occur in the oceans, swamps and rice paddies, can fix nitrogen from the air and thus extend the fertility of the soil.
- C. Lightning imparts sufficient energy to combine the nitrogen and oxygen molecules in its path. The resulting nitrogen oxides are dissolved by rain and absorbed by the soil. It is estimated that between 7 and 10 pounds of nitrogen in the form of nitric acid are added to each acre of soil per year by lightning.

Extensive deposits of sodium nitrate occur in northern Chile. These deposits are an important source of fixed nitrogen. (At one time they were the major source.) The deposits are the residue of centuries-old droppings of birds and form part of the deficient nitrogen cycle.

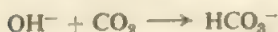
#### 4. PREPARATION OF NITROGEN

Nitrogen and its compounds are studied here in the light of man's quest to fix nitrogen to supplement the cycle and to supply his industrial nitrogen needs without robbing the cycle.

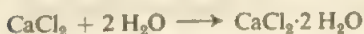
The most obvious source of nitrogen is air. Nitrogen is obtained from air by removing the other gases present or by removing such other gases as are necessary.

- A. A chemical separation of nitrogen from air can be made by passing air successively through a column of sodium hydroxide solution, a drying tube of anhydrous calcium chloride, and then over hot copper (Fig. 21.4).

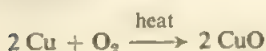
Carbon dioxide is removed in (A) by the reaction:



In passing through (B), water vapor is removed from the gas:



Oxygen is removed by hot copper in the combustion tube (C):



The nitrogen obtained is not pure; examination of Table 21.2 shows that about 1 per cent inert gases remain.

- B. Nitrogen gas, as well as oxygen, is prepared commercially by the fractional distillation of air, as described in Chapter 11. Many tons of the two gases are sold annually in tanks.

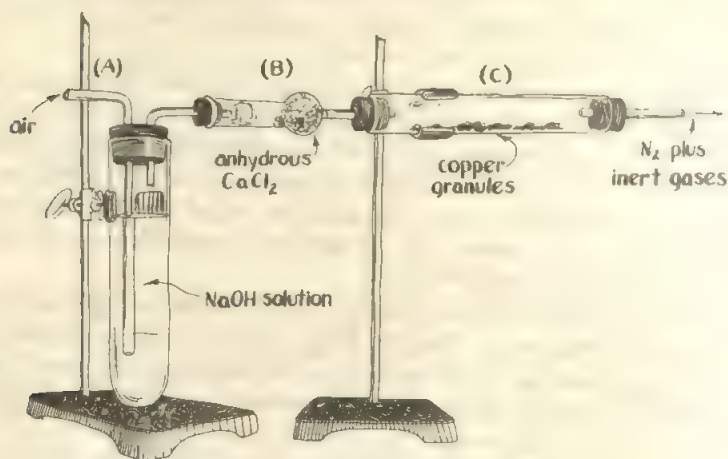
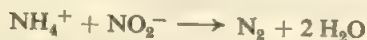
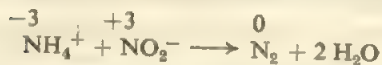


Figure 21.4. Preparation of nitrogen from air.

- C. A small amount of *very* pure nitrogen may be prepared in the laboratory by mixing and heating gently a solution of sodium nitrite and a solution of ammonium chloride:

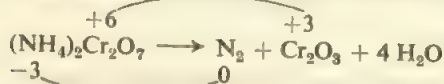


Because solid ammonium nitrite is explosive, the solution is not allowed to evaporate. It decomposes by *auto-oxidation-reduction*. Referring to the equation above and writing oxidation states of nitrogen:



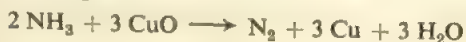
The oxidation state of nitrogen in  $\text{NO}_2^-$  decreases; the nitrogen in  $\text{NH}_4^+$  increases in oxidation state. Ammonium nitrite is its own oxidizing and reducing agent. Auto-oxidation-reduction occurs in many high explosives.

- D. Careful heating of ammonium dichromate yields nitrogen:



A check of changes in oxidation states reveals another case of auto-oxidation-reduction.

- E. When ammonia gas is passed over hot cupric oxide, it is oxidized to nitrogen gas.





### 5. COMPOUNDS OF NITROGEN

A member of Group V of the Periodic Table (and thus possessing 5 valence electrons and a comparatively great electronegativity), nitrogen has an ionic valence of  $-3$  and may exhibit oxidation states from that value up to  $+5$ . The most common oxidation numbers are

- +5  $\text{HNO}_3$ , nitric acid,  $\text{NO}_3^-$ , nitrate ion  
 $\text{N}_2\text{O}_5$ , nitrogen pentoxide
- +3  $\text{HNO}_2$ , nitrous acid,  $\text{NO}_2^-$ , nitrite ion  
 $\text{N}_2\text{O}_3$ , nitrogen trioxide
- 0  $\text{N}_2$
- 3  $\text{NH}_3$ , ammonia,  $\text{NH}_4^+$ , ammonium ion  
 $\text{Mg}_3\text{N}_2$ , magnesium nitride

Other nitrogen compounds with their oxidation states are listed below, the

oxidation number of nitrogen is indicated: nitrogen dioxide,  $\text{NO}_2$ , nitric oxide,  $\text{NO}$ ; nitrous oxide,  $\text{N}_2\text{O}$ ; and hydroxylamine,  $\text{NH}_2\text{OH}$ . Nitric acid, the nitrate salts, ammonia, and ammonium salts are the most important nitrogen compounds. These compounds will be discussed, beginning with ammonia, because ammonia is the starting point in their preparation.

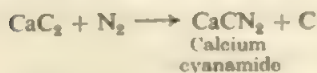
### A. AMMONIA AND AMMONIUM SALTS

### PREPARATION OF AMMONIA, $\text{NH}_3$

- (1) About 1.4 per cent by weight of coal is nitrogen. When coal is "coked," heated in the absence of air, about 20 per cent of the nitrogen is converted to ammonia gas. At one time this was the major source. The need for ammonia, mostly for fertilizers, greatly exceeded the demand, and processes to gain nitrogen from the atmosphere were investigated.
- (2) One successful process to gain  $N_2$  from air is the *cyanamide process*. In this process, calcium carbide obtained by heating a mixture of lime with coke:



is heated with nitrogen to 1000°C in an electric furnace:



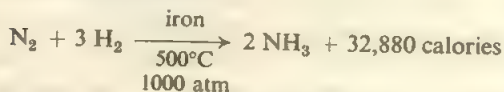
The resulting cyanamide may then be hydrolyzed (by adding water) to ammonia:



or it might be used directly as a fertilizer, hydrolyzing as soil moisture comes in contact with it and releasing the ammonia over a longer period of time. The newer method of nitrogen fixing has replaced the cyanamide process for producing ammonia, but cyanamide is still produced and used as a fertilizer.

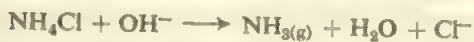
- (3) The *Haber process*, in which the elements comprising ammonia are combined directly, is the important commercial process. It was developed by a German chemist, Fritz Haber, in 1903. The advent of this process was of world-wide historical importance, because Germany, until that time, depended almost entirely on Chilean saltpeter as its source of fixed nitrogen for explosives. Since her supply of saltpeter was cut off because the Allied Powers controlled the seas, Germany could not have waged war for any extended period. But the Haber process, which utilized the nitrogen from the air, made Germany independent of outside sources.

In the Haber process, nitrogen gas from the distillation of liquid air and hydrogen gas from the catalytic reaction of steam with hydrocarbons or with coal are passed over an impure iron catalyst at 500°C and about 1000 atm:

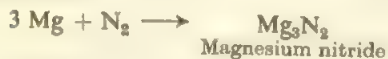


Not more than 60 per cent of the nitrogen and hydrogen can be converted to ammonia at these conditions. The ammonia is liquefied and removed, and the unreacted elemental gases are passed over the catalyst again along with incoming hydrogen and nitrogen. The catalyst is prepared by an elaborate process; it contains at least 95 per cent iron with traces of potassium, aluminum, magnesium and silica. (The Haber process is also discussed in the following chapter on chemical equilibrium.)

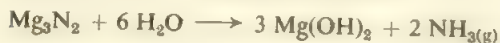
- (4) Ammonia is prepared in the laboratory by adding a strong basic solution to an ammonium salt or solution of that salt.



- (5) An interesting preparation of ammonia involves using nitrogen to support combustion. Magnesium is sufficiently active to burn in nitrogen:



Addition of water releases ammonia:



#### PROPERTIES AND USES OF AMMONIA

Ammonia is a colorless gas with a characteristic odor. It freezes at  $-77^\circ\text{C}$  and boils at  $-33.3^\circ\text{C}$  at a pressure of 1 atmosphere. At greater pressures it is

easily liquefied at room temperature. For this reason it is used in refrigeration. In the refrigerator cycle ammonia (or other gas) is compressed outside the cooling compartment until it is liquefied, giving up the heat of vaporization to the surroundings (Fig. 21.5). The now liquid ammonia is admitted to a container inside the refrigerator where the pressure is released and the liquid vaporizes, taking the heat of vaporization from the surroundings (the inside of the refrigerator). The cycle continues indefinitely, liquefying with pressure

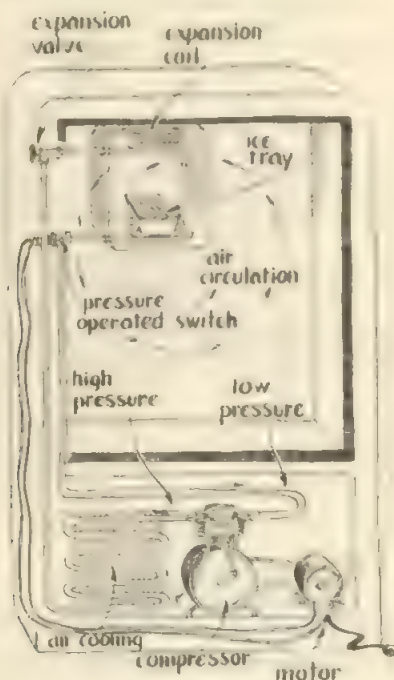
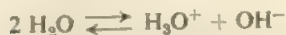


Figure 21.5. Refrigerator cycle.

outside the refrigerator, releasing the heat of vaporization, and vaporizing at reduced pressure inside, taking up the heat of vaporization.

Liquid ammonia (with no water present) is a good solvent and is used as the reacting medium for certain substances that are unstable in water. As a solvent, liquid ammonia resembles water. The ammonia molecules are polar, but not so polar as water. The ionization of ammonia in the liquid is analogous to the ionization of water:

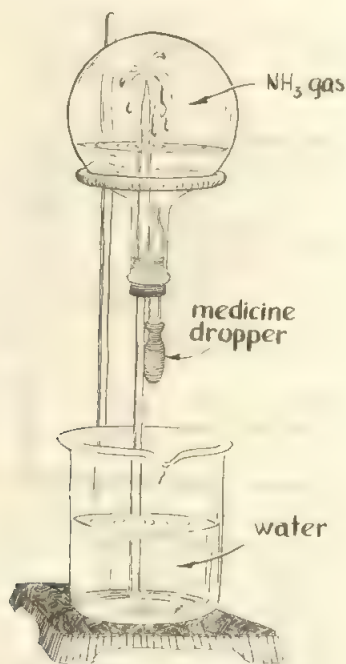


By analogy,  $\text{NH}_2^-$  is the strong basic ion in liquid ammonia and  $\text{NH}_4^+$  is the acid ion. Neutralization transfers a proton to  $\text{NH}_2^-$ . Solutions of  $\text{NH}_4\text{Cl}$

and  $\text{NaNH}_2$  (sodium amide) in ammonia can be titrated with a phenolphthalein indicator.

Ammonia unites with many salts, crystallizing from the liquid as "ammonia of crystallization." Two examples are:  $\text{CaCl}_2 \cdot 2 \text{NH}_3$  and  $\text{ZnCl}_2 \cdot 2 \text{NH}_3$ .

Ammonia is very soluble in water. At room conditions, over 300 L of ammonia will dissolve in 1 liter of water. The rapid solubility can be demonstrated by an ammonia fountain (Fig. 21.6). A glass tube from an inverted

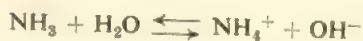


Ammonia Fountain

Figure 21.6. Ammonia fountain.

flask of ammonia gas is immersed in water. A medicine dropper with water is placed through the stopper so that a few drops of water may be admitted to the flask. As soon as the drops of water enter the flask, ammonia dissolves in it, pulling water up into the flask like a fountain.

When ammonia dissolves in water, a weak basic solution results. Spectroscopic data suggest that it is a hydrated ammonia solution and that a small concentration of ammonium ions and hydroxide ions are present by this reaction:



When an ammonia solution is neutralized by an acid, an ammonium salt is left in solution. When ammonia and hydrochloric acid are neutralized and the solution has evaporated, ammonium chloride crystals appear which have



the formula  $\text{NH}_4^+\text{Cl}^-$ . Ammonium chloride is an ionic compound, a salt, as represented by the assigned charges. The ammonium ion is present in many salts, all of which are ionic, behaving very much like corresponding salts of the alkali metals.

Ammonia forms stable complex ions with certain metal ions. A silver ammonia complex results when ammonia solution is added to a silver nitrate solution; an invisible reaction occurs:



This ion is sufficiently stable to dissolve a precipitate of insoluble silver chloride



Addition of ammonia to a pale blue solution of cupric ion changes the color to an intense blue with the formation of a complex ion:



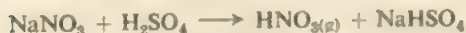
Ammonia is oxidized by air with a platinum catalyst as an intermediate step in the preparation of nitric acid, a major use of ammonia. This reaction will be discussed later.

Ammonia is used directly as a fertilizer. It is also used in making other fertilizers, for example, ammonium nitrate, and in making certain plastics.

## B. NITRIC ACID

### PREPARATION

- (1) For many years, the only method for preparing nitric acid was by distilling the vapor from a mixture of sulfuric acid and Chilean Saltpeter and collecting it in water:

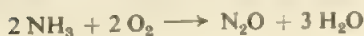
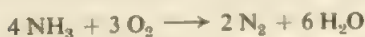


The reaction is not carried farther to obtain more nitric acid:



because, at the temperature required, nitric acid is decomposed. This process is still used, but has become relatively unimportant.

- (2) In the *Ostwald process*, ammonia can be burned with air in the presence of a metal catalyst according to any one of three reactions:



Only the first is of any commercial value. When ammonia is passed with oxygen gas over a platinum gauze catalyst at  $1000^{\circ}\text{C}$ , the combustion to nitric oxide (NO) occurs almost quantitatively, with the time of contact with the catalyst being less than 0.01 second. The catalytic oxidation of ammonia with air can be demonstrated by placing a hot coil of platinum or copper wire above a concentrated ammonia solution in an Erlenmeyer flask (Fig. 21.7). Oxygen in air diffuses into the mouth of the flask to unite with ammonia vapors on the surface of the platinum wire, where the heat of reaction keeps it glowing with a red heat.

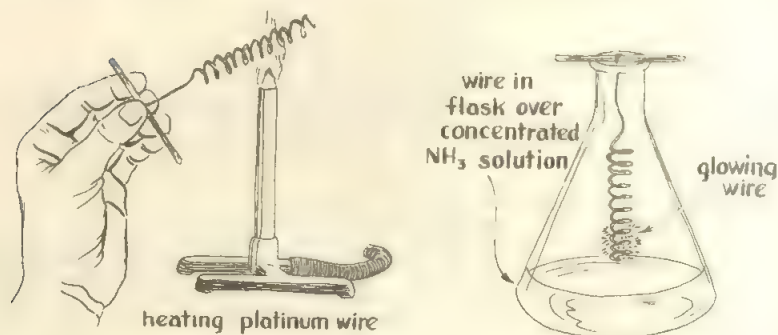
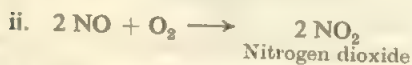
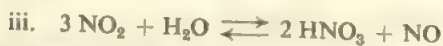


Figure 21.7. Catalytic oxidation of ammonia.

To convert nitric oxide to nitric acid, it is mixed with air and passed upwards through a series of towers down which water is trickling. Two reactions occur in the tower. The first:

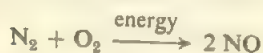


is a slow reaction and no catalyst is known to speed it. The brown gas ( $\text{NO}_2$ ) then dissolves in water.



The nitric oxide released reacts with air and dissolves again. Nitric acid with a concentration of about 55 per cent is prepared by this method.

- (3) Nitric oxide may be prepared from its elements. When a mixture of air enriched with oxygen is passed through a high temperature electric arc, about 2.5 per cent nitric oxide is gained:



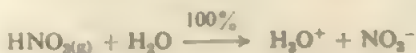
This is the reaction occurring in the path of lightning. In the moist air, the gas is converted to nitrogen dioxide, then to nitric acid. Prior to the Ostwald process, this process was employed in localities where electric power was cheap.

## PROPERTIES AND USES OF NITRIC ACID

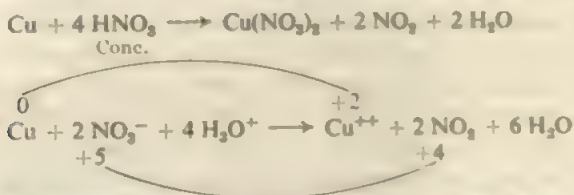
Concentrated nitric acid (about 68 per cent), which is obtained by distilling the acid until it boils at a constant temperature, has a density of 1.42 g/ml. Its molarity is:

$$\frac{1000 \text{ ml/L} \cdot 1.42 \text{ g/ml} \cdot 0.68}{63 \text{ g/mole}} = 15.3 \text{ mole liter} = 15.3 \text{ M}$$

Nitric acid is a strong acid and a good oxidizing and nitrating agent. It ionizes completely in water:



and therefore can be used to neutralize bases. Noble metals such as silver and copper will dissolve in nitric acid, but not in hydrochloric or sulfuric acid. The dissolving is accomplished by an oxidation of the metal



The use of nitric acid with concentrated sulfuric acid as a nitrating agent has been discussed.

## C. NITRATES

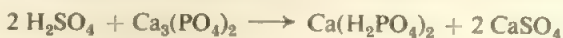
Nitrates are usually soluble in water and may be obtained by crystallization from solution. The nitrate ion is not very stable thermally; any nitrate salt will decompose on heating. At one time the major use of nitrates was in the manufacture of *gun powder*, a mixture which is 75 per cent potassium nitrate, 15 per cent charcoal and 10 per cent sulfur. Nitrate readily supplies oxygen for the rapid burning of charcoal and sulfur to produce a mixture of gases.

When saturated with fuel oil and detonated with dynamite, ammonium nitrate is a high explosive (comparable to the nitro explosives). This chemical is rapidly replacing more costly but no more effective explosives in huge blasting operations. It is also commonly used as a fertilizer.

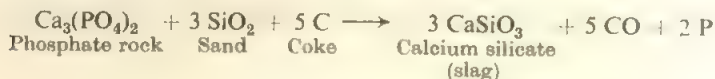
## 6. PHOSPHORUS

As mentioned before, phosphorus occurs in nature as phosphates. One mineral, apatite, has the formula  $\text{Ca}_5(\text{PO}_4)_3\text{F}$ . Some calcium phosphate deposits are of prehistoric animal origin. Calcium phosphate is the mineral matter in bones. Phosphorus is also contained in living cells. The body of an adult human contains about 3.4 pounds of phosphorus. Animals obtain phosphorus from plants. Plants acquire it from the soil. In many soils,

phosphorus is depleted and must be added in fertilizers. The use of concentrated sulfuric acid to convert insoluble phosphate rock to soluble dihydrogen phosphate for fertilizer has been noted:



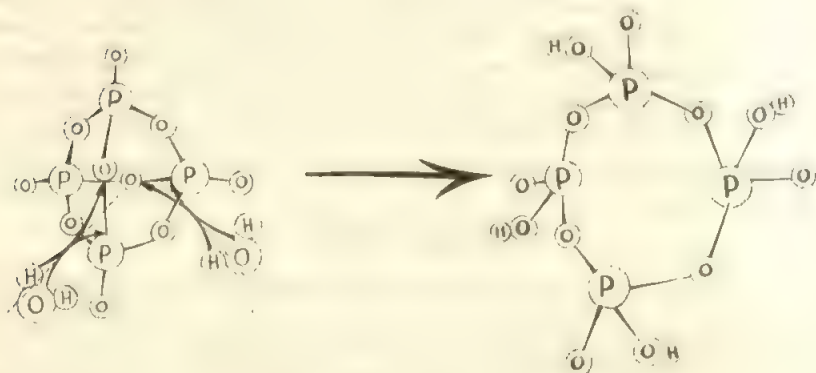
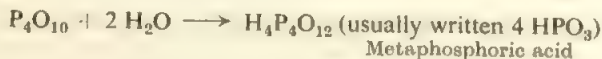
Phosphorus is produced by heating a mixture of phosphate rock, sand and coke in an electric furnace:



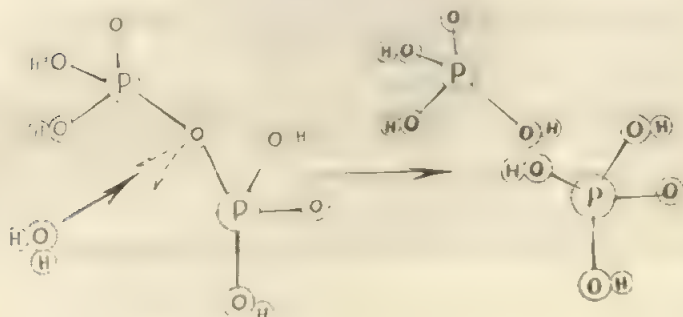
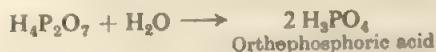
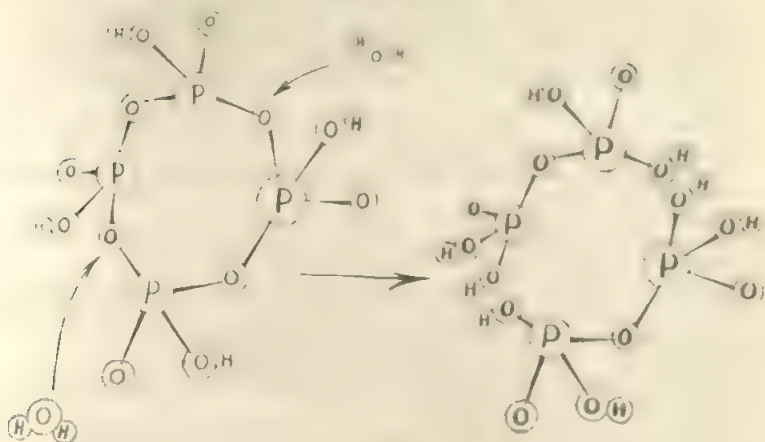
Calcium silicate, called slag, melts and runs to the furnace floor. Phosphorus is vaporized and the vapor is collected in water where it condenses to a liquid. The liquid is poured into molds to solidify. The vapor may be mixed with oxygen in a water-cooled, graphite-lined chamber to form  $\text{P}_2\text{O}_5$ , or  $\text{P}_4\text{O}_{10}$ , directly.

Most of the phosphorus produced is converted into compounds. Large quantities are used in making matches, rat poison and phosphor bronze. Once contained in matches, poisonous white phosphorus has been replaced by phosphorus trisulfide ( $\text{P}_4\text{S}_3$ ), which is in the tip of the match above a mixture of potassium chlorate and sulfur and glue. Friction on the tip ignites the  $\text{P}_4\text{S}_3$ , which, in turn, ignites the sulfur-potassium chlorate mixture.  $\text{KClO}_3$  furnishes oxygen to burn the sulfur. Safety matches in effect have the phosphorus igniting material on the box and the oxidizing-reducing agent mixture on the stick.

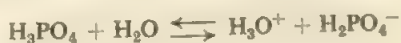
Phosphoric anhydride ( $\text{P}_4\text{O}_{10}$ ) is the anhydride of the three phosphoric acids; they may be prepared by adding varied amounts of water to the oxide:







Orthophosphoric acid is commonly known as phosphoric acid. It is a thick syrupy liquid and a moderately strong acid:



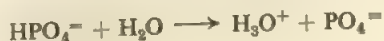
The anion of the sodium salt,  $\text{NaH}_2\text{PO}_4$ , is weakly acidic:



But the anion of disodium hydrogen phosphate is weakly basic. This reaction:



occurs to a greater extent than does this reaction:



## EXERCISES

1. Which element of Group V occurs most abundantly in nature?
2. Which element of Group V is a stable diatomic molecule at room temperature?
3. Which element of Group V is a metal? Which elements are definitely non-metals?
4. Compare the chemical reactivity of white phosphorus, violet phosphorus and nitrogen gas.
5. Explain why white phosphorus is more active to air oxidation than nitrogen gas, and more active than violet phosphorus.
6. Why should white and violet phosphorus differ more in properties than do rhombic and monoclinic sulfur?
7. Describe "active" nitrogen.
8. Which elements of Group V are necessary for plant and animal life?
9. What is the nitrogen cycle?
10. Explain why the element nitrogen is an example of "plenty in the midst of poverty."
11. Describe five ways by which "fixed" nitrogen may be returned or added to the soil.
12. Write equations showing how nitric acid is formed by lightning.
13. How did the development of the Haber process affect world history?
14. Name the four most abundant gases in dry air in the order of decreasing abundance.
15. Explain auto-oxidation reduction.
16. What is the oxidation state of nitrogen in each of the following compounds: (a)  $\text{HNO}_2$ , (b)  $\text{N}_2\text{O}_5$ , (c)  $\text{NO}$ , (d)  $\text{N}_2\text{O}$ , (e)  $\text{NO}_2$ , (f)  $\text{N}_2\text{O}_4$ , (g)  $\text{HNO}_3$ ?
17. Describe the Haber process.
18. Write equations (in two steps) for the preparation of ammonia gas using magnesium.
19. How does liquid ammonia resemble water as a solvent?
20. Explain the cycle occurring in the cooling system of a refrigerator.
21. Describe the Ostwald process for producing nitric acid.
22. How is nitric acid made from Chilean saltpeter?
23. What is the major use of ammonia?
24. What two important properties does sulfuric acid possess that nitric acid does not possess. What property does nitric acid have that is not exhibited by cold dilute sulfuric acid?
25. How is the element phosphorus produced?
26. Name the uses of phosphorus.
27. Name the anhydride of the phosphoric acids.
28. How do the phosphoric acids differ from one another structurally?

RATES OF REACTION  
AND EQUILIBRIUM

Two questions of utmost importance in chemical processing are, "How much?" and "How long?"

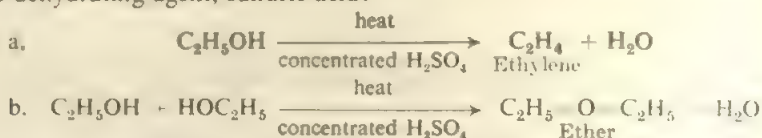
The first question may be stated more correctly, "What proportions of the reactants (the raw materials) may be converted to saleable products?" Although the best purification processes tend to concentrate most of the impurities with the least amount of product to be thrown away, there are always losses incurred in the purification of products. Some losses are due to spillage and improper handling, but even washing solutions carry some of the product away with the impurities.

But even if none of the products were lost in handling and in purification, one cannot expect to obtain 100 per cent products, because many reactions, by their nature, do not "go to completion"; that is, the reaction proceeds until a certain per cent of the reactants are converted to products; it attains "equilibrium" and stops. As long as the conditions are not varied, the reaction proceeds no further. For example, it has been noted that only 60 per cent of nitrogen and hydrogen in the correct proportions with a catalyst at 500°C and 1000 atmospheres pressure may be converted to ammonia. Furthermore, this percentage is best for the process and was attained only by understanding equilibrium and its dependence on reaction conditions.

The question "How long?" may also be expanded: "How long will it take for the reactants, or a certain percentage of the reactants, to be converted to the desired products?" Time is at a premium in our economy. If one were to prepare hydrogen in the laboratory, he would use zinc metal and hydrochloric acid instead of magnesium and hot water. Both reactions yield pure hydrogen in very good percentages, but the first process yields in minutes the amount of gas gained from the second process in hours. Time is of particular significance for reactions carried out at elevated temperatures,

because fuel is required to maintain the temperature. If certain reactions took hours, and not seconds, the fuel costs would be prohibitive.

Often there are competing reactions. Both ethylene, a component of natural gas, and diethyl ether, an anesthetic, are made by heating ethyl alcohol with the dehydrating agent, sulfuric acid:



The desired product, the ether, can be gained in good yield by varying conditions, for example, by increasing the rate of reaction b to a much greater extent than reaction a.

The two questions "How much?" and "How long?" are related; the state of equilibrium depends on the rate.

## 1. THE RATE OF A REACTION

A chemical reaction has previously been defined as a change in atomic groupings: ions may be formed or changed to atoms or molecules; molecules may be broken down or formed. Regardless of the exact nature of the atomic grouping, in a chemical reaction a substance (or substances) with definite physical properties disappears and a substance (or substances) of different definite properties appears.

One can follow the course of a reaction either by watching how fast a reactant disappears or by watching how rapidly a product appears and increases in amount. One chooses the product or reactant whose amount of increase or decrease is easiest to observe. If a gas is evolved from liquids one can watch the bubbling to see how fast the reaction is proceeding, or collect the gas above the reaction and note the rate of increase in volume. If a colored product is formed, one can note the change in color as time elapses. If heat is evolved (that is, if the reaction is *exothermic*) one can follow the reaction by measuring the heat liberated.

The rate of a reaction may be expressed in different terms. The chemist may be concerned with the moles of reactant disappearing or with the moles of product appearing per second; or he may be concerned with the change in concentration (that is, the change in moles per liter per second). A clearer distinction between the terms will be attempted later in the chapter, and various important conditions that change the rate of a reaction will be discussed from both the experimental and the theoretical standpoints.

### A. TEMPERATURE

It is common knowledge that changes in temperature affect the rate of chemical reactions; an increase in rate always accompanies an increase in temperature. By placing food on a burner or in a hot oven, the housewife initiates many complicated chemical reactions that do not occur at room



temperatures. If certain foods do not cook satisfactorily at the temperature of boiling water, the housewife may place them and the water in a pressure cooker, where higher temperatures can be attained. The housewife slows some chemical reactions when she places food in the refrigerator, and she stops them almost completely when she puts food in a freezer.

As a general rule, the rate of a chemical reaction is "doubled" by a temperature increase of only  $10^{\circ}\text{C}$ . The term "doubled" is used loosely here. Some reaction rates are doubled, whereas others are tripled and still others

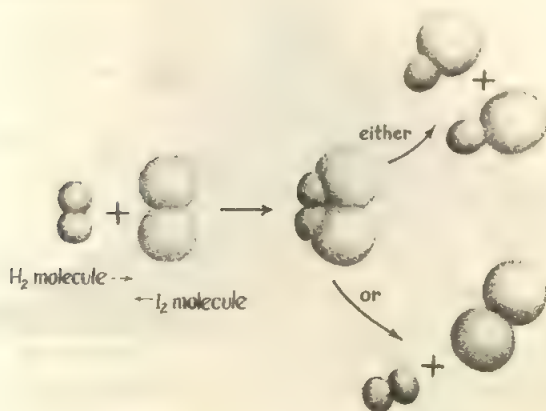
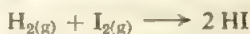


Figure 22.1. Reaction of  $\text{H}_2$  and  $\text{I}_2$ .

are increased only by half. Since a small change in temperature has such a great effect on the reaction rate, kitchen ovens and other apparatus involved with chemical reactions must have precise temperature controls.

An interesting example of the change in reaction rate with temperature is found in the rate of development and metabolism of so-called "cold-blooded" animals. (Cold-blooded animals are those that assume the temperature of their surroundings.) A tadpole develops two to three times faster in water at  $20^{\circ}\text{C}$  than he does in water at  $10^{\circ}\text{C}$ . The metabolic processes of reptiles are more than doubled with a  $10^{\circ}\text{C}$  rise in temperature. Warm-blooded animals maintain a set body temperature so that external changes in temperature have little or no effect on reaction rates within the body.

To understand the effect of temperature on the rate of reaction, consider one of the simplest of reactions, that of hydrogen gas and iodine vapor at high temperature ( $700^{\circ}\text{A}$ ) to form gaseous hydrogen iodide:



Exhaustive studies have shown that this reaction is a simple bimolecular reaction. That is, two molecules, one of each reactant, collide and then separate into molecules of product. The reaction is visualized in Figure 22.1.

The two stable gas molecules, one of hydrogen and one of iodine, each with an inert gas configuration, must collide together at just the right angle and with sufficient force to upset electron orbits completely. When orbits re-form, unlike atoms may be paired together and the product hydrogen iodide is formed. At suitable reaction temperatures only a very, very small fraction of the molecular collisions yields products. Certain conditions must be met:

- (1) The molecules must hit broadside. The opposite atoms must be close enough to form two molecules.

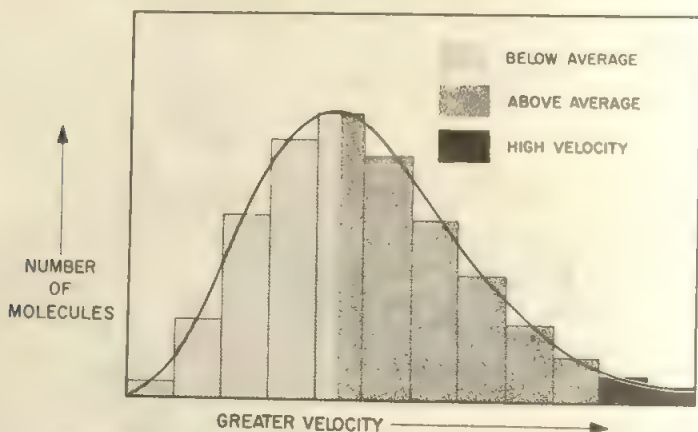


Figure 22.2. Relative velocity distribution among molecules.

- (2) The collisions must be between two very rapidly moving molecules. Molecules with negative shells of electrons repel one another. To react, molecules must have sufficient energy to overcome the repulsion, to collide and to shatter the existent covalent bonds.

When the deformed molecules seek to regain stability, they may form the original stable molecules or those of the product.

If all collisions between hydrogen and iodine vapor molecules were successful (or if a very large fraction were successful) in forming hydrogen iodide, the reaction would be so fast that the gases would explode.

Remember that all molecules of a gas do not have the same translational energy. At any one instant, due to random collisions with one another, few molecules have very low energy (velocity), many have a velocity very nearly average, and another few have very high energies (Fig. 22.2). Only high energy molecules (represented by the dark bars to the far right on the graph) can collide with sufficient force to react. If a molecule of hydrogen, the instant it has very high energy, collides at just the right angle with a molecule of iodine vapor, at its instant of high energy, two molecules of hydrogen iodide *may* be formed. No other collisions can result in the product.

Only *high energy molecules* propagate the chemical reaction; molecules of

low or near average velocity cannot react. Two high energy molecules (one hydrogen and one iodine) must find one another before they collide with other molecules and are thereby reduced to low energy molecules. The temperature of the gases determines the fraction of high energy molecules. The Kinetic Theory tells us that the average translational energy is proportional to the

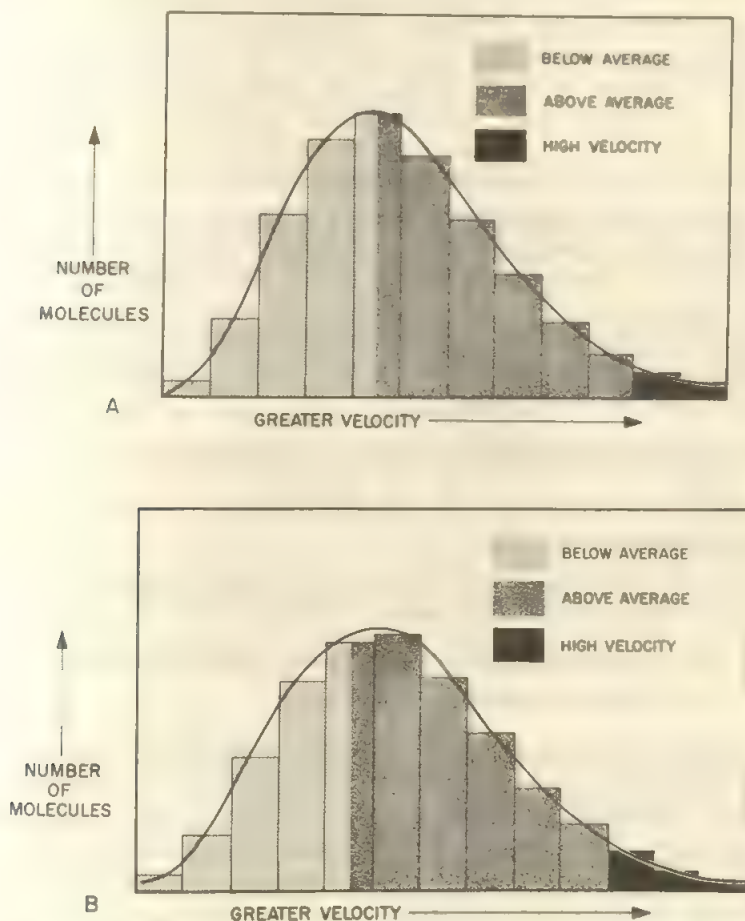


Figure 22.3. Relative distribution of molecular velocities at two temperatures.

a. at  $T_1$

b. at  $T_2$

$T_2 > T_1$

absolute temperature. Likewise, at any set temperature, at any instant, a set fraction of the molecules are sufficiently energetic for reaction.

**Effect of Temperature on Rate.** Why should the rate of reaction of hydrogen and iodine vapor double when the temperature is raised from  $700^\circ\text{A}$  to  $710^\circ\text{A}$ ? The energy due to the velocity of the molecules is increased by  $1/70$ , but this increase cannot double the rate. A few more collisions occur per second, but this cannot double the reaction.

The answer lies in the fact that the *number of high energy molecules is doubled* (Fig. 22.3). At the higher temperature there are still only a few molecules with enough energy to react, but this few is twice as many as before.

### B. CONCENTRATION

An increase in the concentration of one or all the reactants in a reaction mixture increases the rate of reaction. Advantage is taken of this fact when the mixture of air and gasoline vapor is compressed in an automobile engine cylinder. A sharper explosion results. Steel wool burns only slowly in the heat of a bunsen flame in air, but it burns with a brilliant white flame in pure oxygen, whose oxygen concentration is five times greater than that of air. A 1 molar hydrochloric acid solution reacts much faster than 1 molar acetic acid, because the concentration of the active component of the solutions, the hydronium ion, is almost 1000 times greater. Silver precipitates on a copper wire much faster from a 1 molar solution of silver nitrate than from a one-half molar solution.

Returning to the one step reaction between hydrogen and iodine vapor, experience has shown that the rate of the reaction in moles per liter per second is given by the equation:

$$\begin{aligned}\text{moles of H}_2 \text{ lost/liter/second} &= \text{moles of I}_2 \text{ lost/liter/second} \\ &= k_1 \times [\text{H}_2] \times [\text{I}_2]\end{aligned}$$

In this equation:

- i.  $k_1$ , a number, is equal to the moles/liter lost per second when hydrogen gas and iodine vapor are at 1 mole/liter.
- ii.  $[\text{H}_2]$  means moles/liter of hydrogen in the reaction mixture.
- iii.  $[\text{I}_2]$  means moles/liter of iodine vapor.

In simple terms this equation says that the rate of reaction is proportional to the moles per liter of hydrogen and the moles per liter of iodine vapor. If either concentration increases, the reaction goes faster. In fact, if one concentration is doubled, the rate doubles; if both concentrations are doubled, the reaction proceeds four times as fast. *This is true only if the temperature is not allowed to change.*

A simple analogy might be helpful in understanding the variation of reaction rate with concentration. Suppose 100 pairs of boys are walking about at random on the campus. At the same time 100 pairs of girls are walking at random on the same campus. It is springtime. Each time a pair of boys meets a pair of girls, a reaction occurs, the grouping changes. Suppose that in 20 minutes, 10 pairs of boys meet 10 pairs of girls and 20 couples are formed.

Now suppose that 200 pairs of boys and 100 pairs of girls start walking at random on the campus. How long will it take for 20 couples to be formed. Obviously with twice as many boys looking, it should take half the time, 10 minutes.



But if there are 200 pairs of boys and 200 pairs of girls at the beginning each one of twice as many boys will be looking for any one of twice as many girls and only 5 minutes will be required for the first 20 couples to be formed.

Notice only the initial rate of reaction was considered (the first 20 couples); no mention was made of the time for all couples to be paired off. For as a reaction proceeds the concentration of reactants decreases and the reaction slows down accordingly. This agrees with the rate equation.

No mention was made of the concentration of the products. The amount of product does not affect the rate, except that an increase in product concentration means a decrease in the reactants.

### C. THE STATE OF SUBDIVISION

A heterogeneous reaction is one occurring between substances in two different states or phases. In heterogeneous reactions the state of subdivision of one or more of the reactants is very important.

Powdered sugar dissolves much faster in water than granular sugar. This is a physical reaction, but it is similar to some chemical reactions. It is obvious that in this case much more crystal area, and therefore many more sugar molecules, are at the water's edge, ready to dissolve.

Two immiscible liquids react much more rapidly when they are shaken vigorously. The liquids are broken into fine droplets mixed together in a temporary emulsion. A much greater area of contact exists between molecules of the two liquids than existed when one liquid lay stationary above the other.

Silver metal precipitates from a silver nitrate solution much more rapidly on fine copper metal shreds than on one large copper wire of the same weight. Again, a much greater area of copper is in contact with the silver-bearing solution. The rate equation for this reaction at a set temperature is of this form:

$$\text{Rate} = k \times \text{area} \times [\text{Ag}^+]$$

The rate increases directly with the concentration of the silver ion and also directly with the surface area of copper in contact with the solution. The rates of certain reactions are affected spectacularly by changes in the state of subdivision of the reactants. A lighted match dropped into an open pan of gasoline is extinguished by the liquid. But a spray of the liquid (tiny droplets in air) explodes with the slightest spark. Chunks of coal ignite only when placed in an open flame at or above the kindling temperature, a temperature barely attained by vigorously burning wood. On the other hand, fine coal dust mixed with air is a dangerous explosive. Coal mine surfaces are saturated with water before blasting to prevent coal dust explosions. Structural aluminum melts in the heat of a crashed and burning airplane, but aluminum dust explodes in air when ignited.

Explosions occur for these reasons: (a) The substance can be oxidized in air. (b) A great surface area is available between the combustible material and the air. (c) The air and combustible material are well-mixed and in the right proportions so that neither the material nor the oxygen will be left unreacted

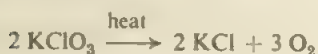
because the other has been consumed. (d) Furthermore, the combustion reaction is highly exothermic so that when one tiny volume of combustible dust and air is heated to kindling temperature by a spark and burns, sufficient heat is liberated to raise the mixture immediately around it to kindling temperature. Thus the combustion sphere expands to include the ever growing preheated shell and an explosion results.

While the fine state of subdivision of the combustible material and the proper mixing of the material with air are sufficient to cause an explosion when ignited, temperature effects are unescapably involved, as also are concentration effects in the compressed preheated area into which the explosion progresses.

#### D. CATALYSIS

Catalysts are of great importance in chemical processing. Many processes become practicable only by addition of a catalyst:

- (1) Potassium chlorate decomposes very slowly into potassium chloride and oxygen at 400°C when pure:

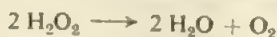


At the same temperature the salt is changed, and more rapidly, to potassium perchlorate:



When a trace of manganese dioxide is added, decomposition to give oxygen occurs rapidly and almost completely at 200°C.

- (2) Addition of a few drops of copper sulfate solution to a sluggish mixture of zinc metal and sulfuric acid causes it to bubble vigorously with the now rapidly escaping hydrogen.
- (3) Ammonia gas burns very poorly, if at all, in air, but on the hot surface of a platinum wire, ammonia and oxygen of the air unite almost instantaneously. This is the important step in the Ostwald process.
- (4) Liquid vegetable oil may be shaken endlessly with hydrogen gas with no result. But when finely divided nickel or platinum is added, hydrogen is adsorbed. The oil is converted to a fat for making shortening or butter substitutes.
- (5) When a pinch of manganese dioxide is added to a solution of hydrogen peroxide, bubbling occurs as oxygen is released:



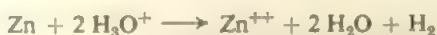
The same result is obtained by adding a drop of blood.

The extra substances added in the examples cited above, copper sulfate solution, platinum wire, finely divided nickel, manganese dioxide, and catalase, a component of blood, are catalysts. They possess three traits in common. (a) Each increases the rate of a reaction. (b) Each can be recovered unreacted at the termination of the reaction. (c) Each is specific for a certain

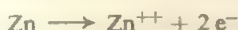
reaction. That is, the catalyst does not increase the general reactivity of a substance or substances, but increases one special reaction. For example, addition of manganese dioxide speeds the decomposition of hot potassium chlorate to form oxygen, but has no effect on the rate of formation of potassium perchlorate. Catalase in blood differs from the other catalysts in that it is produced in the body. It is called an enzyme.

The five examples of catalysis represented here were chosen for variety. There are many more catalyzed reactions and many more kinds of catalysts. The functions of many catalysts are not understood. Certainly they do not all behave alike. Reasonable explanation of the operation of some catalysts are known; three will be given here:

When copper sulfate solution is added to a mixture of mossy zinc and sulfuric acid in which this reaction is slowly taking place:



copper, being less active than either zinc or the hydronium ion, "plates-out" in spots on the zinc metal surface. Tiny voltaic cells are then set up between the dissimilar metals in solution. The zinc metal surface in the solution acts as the anode, and zinc atoms dissolve from the surface, leaving electrons behind:



The electrons are conducted through the zinc to a copper spot, cathode, where the hydronium ions can accept electrons more easily and hydrogen gas is formed.



Cell reactions of this type account for the fact that aluminum that is 99 per cent pure corrodes in sea water, whereas very pure electrolytically refined aluminum does not.

Platinum metal, the catalyst for the hydrogenation of vegetable oils and for many other hydrogenation reactions, is called a contact catalyst. It appears that reactants must come in contact with the surface of the catalyst. As evidence, platinum is much more efficient when used in finely divided form precipitated in a thin layer on the surface of pumice or other inert material. Hydrogen is very tightly adsorbed on platinum; it appears to penetrate in between the platinum atoms in the metal lattice. In fact, at high temperatures (300°C) hydrogen will pass slowly through a solid platinum sheet. As the molecules vibrate more rapidly, the hydrogen *atoms* can pass from hole to hole in the crystal. (The spaces between the metal atoms are too small to accommodate molecules.) One can reason that collisions of "hydrogen hungry" molecules with free hydrogen atoms held securely and separately at the surface might be more productive than collisions of the free molecules. Contact catalysts are easily "poisoned." If impurities collect on the "active" surface, the catalytic action is "killed."

## E. INHIBITORS

Some authors define a catalyst as a substance which alters the rate of reaction. This definition can include both positive catalysts, which increase the rate of reaction, and negative catalysts, which cause reactions to proceed more slowly. We choose to call the so-called negative catalysts *inhibitors*. Acetanilide is added to hydrogen peroxide to suppress release of oxygen. Antioxidants retard the oxidation of butter to keep it fresh. Stabilizers keep explosives safe in handling. Antiknock agents cause gasoline-air mixtures to burn more slowly at high pressure. All these are inhibitors.

Although other factors affect the rate of reaction to a lesser extent (and to a large extent in special reactions), temperature, concentration (pressure), state of subdivision and catalysis are most important.

## 2. CHEMICAL EQUILIBRIUM

## A. EXPERIMENTAL

The existence of equilibrium might be best understood by considering a series of experiments that might be carried out in the laboratory, with the results given below.

**Experiment 1.** A 1 liter quartz glass vessel containing 0.01 mole  $H_2$  and 0.01 mole  $I_2$  is placed in a furnace at  $425^\circ C$ . After several hours, the flask is removed, "chilled" to room temperature to stop all reaction and analyzed. It is found to contain:

0.00214 mole  $H_2$  ( $2.14 \times 10^{-3}$  mole)

$2.14 \times 10^{-3}$  mole  $I_2$

and 0.0157 mole HI

**Experiment 2.** A 1 liter vessel containing 0.02 mole of HI gas is placed in the same furnace at the same temperature. After several hours, and after chilling, an analysis shows it to contain:

$2.14 \times 10^{-3}$  mole  $H_2$

$2.14 \times 10^{-3}$  mole  $I_2$

and 0.0157 mole HI

**Experiment 3.** A 1 liter flask containing either 0.01 mole of  $H_2$  and 0.01 mole  $I_2$  or 0.02 mole HI is placed in a furnace at  $420^\circ C$  for several hours, chilled and analyzed. Analysis reveals the presence of slightly *more than*:

0.0157 mole of HI

and *less than*

$2.14 \times 10^{-3}$  mole of each  $H_2$  and  $I_2$



**Experiment 4.** A 1 liter flask containing either 0.01 mole  $\text{H}_2$  and 0.01 mole  $\text{I}_2$  or 0.02 mole  $\text{HI}$  is placed in a furnace at 430 C for several hours, chilled and analyzed. Analysis reveals the presence of slightly *less than*

0.0157 mole of  $\text{HI}$

and *more than*

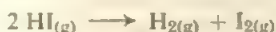
$2.14 \times 10^{-3}$  mole of each  $\text{H}_2$  and  $\text{I}_2$

None of these four experiments reveals any rates of reaction. In each case the reaction has progressed until all changes in concentration have come to a standstill.

If when iodine vapor and hydrogen gas only are placed in a container at 425 C (Experiment 1) hydrogen iodide is formed, this reaction must occur:



If when hydrogen iodide is placed alone in a container at 425°C for several hours (Experiment 2) analyses show that hydrogen and iodine are both present, this reaction must occur:



But these reactions are opposites. It might be supposed that if one reaction occurs, the other cannot. However, notice that regardless of the beginning amounts, the system attains the same final state:  $2.14 \times 10^{-3}$  mole of  $\text{H}_2$ ;  $2.14 \times 10^{-3}$  mole of  $\text{I}_2$ , and  $1.57 \times 10^{-2}$  mole of  $\text{HI}$ . Furthermore, one can alter the percentages of gases in the sealed container by raising or lowering the temperature (Experiments 3 and 4).

Such a reaction that can proceed in either direction is written in this manner with double arrows,



and is said to be *reversible*. When gases in the system described in Experiment 1 and Experiment 2 reach a constant state with no further changes in concentration, the system is said to be in *equilibrium with respect to the reversible reaction*.

Because equilibrium can be attained from either set of reactants, and because a change in temperature changes the equilibrium concentration, it seems obvious the *state of equilibrium is not static but dynamic*. In other words, 0.01 mole of hydrogen and 0.01 mole iodine vapor do not react in a liter vessel until  $2.14 \times 10^{-3}$  mole of each remain and *then suddenly stop*. Nor does 0.02 mole of hydrogen iodide react until only 0.0157 mole remains and *then suddenly stop*. In both cases the reaction continues as long as the system is kept at a sufficient temperature for an appreciable reaction. The reaction slows as the reactant concentration decreases, but it appears to stop at equilibrium only because the product(s) react together, opposing the reaction. When both reaction rates are the same, the concentrations cease to change.

## B. RATE EQUATIONS IN EQUILIBRIUM

In a previous section the rate equation for this reaction:



occurring at any set temperature was said to be of this form:

$$\text{Rate } (\longrightarrow) = k_1[\text{H}_2][\text{I}_2]$$

Following the same reasoning, the rate equation for the decomposition of hydrogen iodide gas:



$$\text{Rate } (\longleftarrow) = k_2[\text{HI}]^2$$

where  $k_2$  is some number and  $[\text{HI}]$  is the concentration of hydrogen iodide in moles per liter.

Because two molecules of hydrogen iodide must collide to form a hydrogen and an iodine vapor molecule, the rate of the reaction is proportional to the hydrogen iodide concentration squared. If the concentration of hydrogen iodide were doubled, the rate equation states that the reaction rate would be increased fourfold. In other words, twice as many molecules would have twice the chance of colliding with another.

The arrow for the rate equation for the decomposition of hydrogen iodide was written in the reverse direction to indicate that it represents the reaction which is the reverse of the combination of hydrogen and iodine vapor.

Now consider the events that occur in the quartz flask in Experiment 1 (page 332), beginning with the moment it is placed in the furnace. At first,  $\text{H}_2$  and  $\text{I}_2$  combine rapidly to form hydrogen iodide:

$$\text{Rate } (\longrightarrow) = k_1 0.01 \times 0.01 = k_1 \times 10^{-4}$$

There is no reverse rate at the beginning, because no HI molecules are present and the concentration of hydrogen iodide is zero. The rate equation agrees:

$$\text{Rate } (\longleftarrow) = k_2 \times 0^2 = 0$$

As the forward reaction proceeds, consuming  $\text{H}_2$  and  $\text{I}_2$ , the forward rate decreases, HI appears and the reverse rate begins, slowly at first, but increasing rapidly as more HI is produced. When the hydrogen and iodine concentrations drop to one-half the initial value, the rate equations are:

$$\text{Rate } (\longrightarrow) = k_1 \times 0.005 \times 0.005 = 2.5 \times 10^{-5} k_1$$

and

$$\text{Rate } (\longleftarrow) = k_2(0.01)^2 = 10^{-4} k_2$$

The rates are not equal; the experimental results show that equilibrium is not attained until about three fourths of the reactants are converted to products. It just happens that  $k_2$  is a much smaller number than  $k_1$ . Finally

as the forward rate decreases with the falling concentrations of  $\text{H}_2$  and  $\text{I}_2$ , and as the reverse rate increases with rising  $\text{HI}$  concentration, the two rates become equal and equilibrium is attained. The diagrams in Figure 22.4 show how the rates of the forward and reverse reactions change with time and how the concentration of reactants and products varies in Experiment 1.

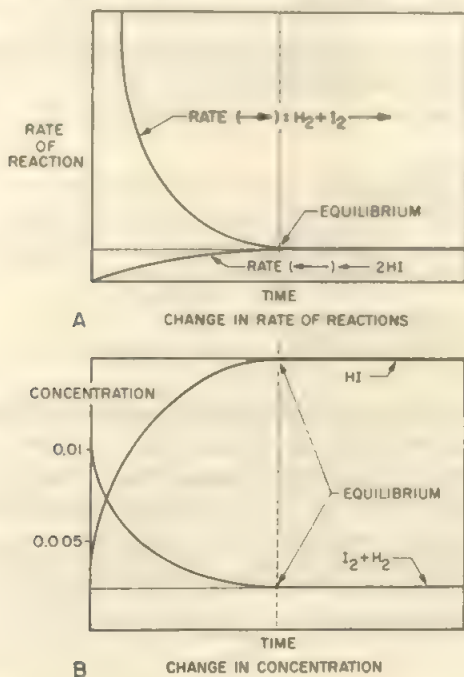


Figure 22.4.

At equilibrium, the concentrations cease to change and  $\text{Rate}(\rightarrow) = \text{Rate}(\leftarrow)$ . This is a necessary condition for equilibrium. The equation becomes very useful when one substitutes the rate expressions:

$$k_1[\text{H}_2][\text{I}_2] = k_2[\text{HI}]^2$$

The equation might be written more correctly in this manner:

$$(X) \quad k_1[\text{H}_2 \text{ eq}][\text{I}_2 \text{ eq}] = k_2[\text{HI eq}]^2$$

because unless the concentrations are those of an equilibrium mixture, the equality does not hold.

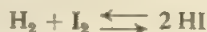
Equation (X) is the first of three statements that will be used later in discussing the effect of changes in different conditions on equilibrium concentrations.

### C. THE MASS LAW EQUATION

In any reversible simple process at equilibrium:

$$\text{Rate}(\rightarrow) = \text{Rate}(\leftarrow)$$

For the reaction:



it follows that:

$$k_1[\text{H}_2 \text{ eq}][\text{I}_2 \text{ eq}] = k_2[\text{HI eq}]^2$$

when  $k_1$  and  $k_2$  are rate constants for the forward and reverse reactions respectively at a certain temperature.

A simple mathematical rearrangement reveals that:

$$\frac{k_1}{k_2} = \frac{[\text{HI eq}]^2}{[\text{H}_2 \text{ eq}][\text{I}_2 \text{ eq}]}$$

Using the equilibrium concentration values from Experiment 1 one can evaluate the ratio of  $k_1$  to  $k_2$ .

$$\frac{k_1}{k_2} = \frac{(0.0157)^2}{(2.14 \times 10^{-3})^2} = 53.9$$

One might have expected  $k_1$  to be much larger than  $k_2$  because at equilibrium only low concentrations of  $\text{H}_2$  and  $\text{I}_2$  ( $2.14 \times 10^{-3}$  mole/liter in this equilibrium mixture) are required to produce HI as fast as it is used up from a much higher concentration ( $1.57 \times 10^{-2}$  mole per liter for this case).

The ratio of the rate constants is more important in chemistry than the individual rate constants and is given a symbol and a name:

$$\frac{k_1}{k_2} = K \text{ eq, the Equilibrium Constant}$$

Again:

$$(Y) \quad \frac{[\text{HI eq}]^2}{[\text{H}_2 \text{ eq}][\text{I}_2 \text{ eq}]} = K \text{ eq}$$

$K \text{ eq}$  is a number that changes only when temperature is changed. Regardless of the total pressure of gases in the vessel and regardless of initial gaseous concentrations, the value of the constant does not change. A second determination of  $K \text{ eq}$  may help to emphasize that fact.

**Experiment 5.** 0.10 mole of  $\text{H}_2$  and 1.24 moles of HI are admitted to a previously evacuated 10 liter flask, placed in a furnace at  $425^\circ\text{C}$ , left for several hours, chilled and analyzed. The analysis revealed the presence of the following amounts: 0.20 mole  $\text{H}_2$ , 0.10 mole  $\text{I}_2$ , and 1.04 moles HI, all in the 10 liters.

Substituting the individual concentrations in moles per liter in the Mass Law Equation, one obtains

$$\frac{[\text{HI eq}]^2}{[\text{H}_2 \text{ eq}][\text{I}_2 \text{ eq}]} = \frac{(0.104)^2}{0.020 \times 0.010} = 54.0 = K \text{ eq}$$

The value of  $K \text{ eq}$  (54.0) agrees well with 53.9 determined above.



## D. LE CHATELIER'S PRINCIPLE

Equation (Y), the Mass Law Equation, is the second of three statements that will be used to illustrate the effect of changing conditions on equilibrium concentrations. The third statement is non-mathematical; it was uttered by a great French chemist, Henri Louis Le Chatelier (1850-1936): "*When a stress is applied to a system in equilibrium, the system tends to rearrange itself so as to nullify the stress.*" Stresses are changes in conditions which affect equilibrium. The meaning of the statement will be clarified as it is applied in the qualitative discussion to follow.

## E. THE EFFECT OF CHANGES IN TEMPERATURE ON THE CONCENTRATIONS OF PRODUCTS AND REACTANTS AT EQUILIBRIUM

Consider an equilibrium mixture of the three gases at a set temperature, for example, at 425°C. At equilibrium:



and



are equal and

$$k_1[\text{H}_2][\text{I}_2] = k_2[\text{HI}]^2$$

That is, because  $k_1$  and  $k_2$  have set values at that temperature, the three concentrations have already adjusted themselves through reaction until the equality holds. The concentrations are equilibrium concentrations and the equation may be written:

$$k_1[\text{H}_2 \text{ eq}][\text{I}_2 \text{ eq}] = k_2[\text{HI eq}]^2$$

Now suppose the temperature of the gas mixture is raised from 425°C to 430°C. *All reaction rates are increased with an increase in temperature*, and therefore both the forward and reverse rates are increased. The rate increases appear as increased values of  $k_1$  and  $k_2$  in the rate equation. Should the forward and reverse rates be increased to the same extent (should  $k_1$  and  $k_2$  increase in the same proportion), equilibrium would be maintained, with no change in concentrations. This happens for some *few* reactions. In general, for reasons that will become apparent, one rate (forward or reverse) is increased more than the other, equilibrium is upset and an adjustment in concentrations follows to restore it.

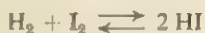
In reference to Experiment 4, page 333, for this particular reaction  $k_2$  is increased more than  $k_1$  by raising the temperature to 430°C from 425°C, since less hydrogen iodide is found in the final gas mixture. Pertinent to the discussion is the fact that the reaction of hydrogen and iodine vapor is exothermic. When several moles of hydrogen and several moles of iodine vapor are placed together and allowed to react at 425°C until 2 moles of hydrogen iodide are formed, 3000 calories of heat are liberated. It follows

that when 2 moles of hydrogen iodide decompose to 1 mole of hydrogen and 1 mole of iodine vapor, 3000 calories are absorbed.

Apply Le Chatelier's Principle to this system. When heat is added to an equilibrium mixture of hydrogen, iodine vapor and hydrogen iodide, raising the temperature from 425° C to 430° C, the system tries to nullify the stress, i.e., it tries to hold the temperature down. The system must absorb calories. This it can do if hydrogen iodide is converted to hydrogen and iodine vapor. Experiment 4 shows that some hydrogen iodide is converted to the elements, because that concentration decreases while the other concentrations increase. The stress is not nullified, but the system tries to nullify it.

#### F. THE EFFECT OF A CHANGE IN ONE OR MORE CONCENTRATIONS ON OTHER EQUILIBRIUM CONCENTRATIONS

Consider the rate expressions for the reactions:



$$k_1[\text{H}_2][\text{I}_2] \text{ and } k_2[\text{HI}]^2$$

At equilibrium:

$$k_1[\text{H}_2 \text{ eq}][\text{I}_2 \text{ eq}] = k_2[\text{HI eq}]^2$$

If additional hydrogen iodide is added:

$$k_1[\text{H}_2][\text{I}_2] < k_2[\text{HI}]^2$$

The notation "eq" is dropped for there is no equilibrium. HI is being consumed faster than it is forming, while  $\text{H}_2$  and  $\text{I}_2$  are being formed faster than they are being consumed. Therefore:

Rate ( $\longrightarrow$ ) increases as  $[\text{H}_2]$  and  $[\text{I}_2]$  increase

Rate ( $\longleftarrow$ ) decreases until equilibrium obtains

Addition of HI has increased the concentration of both  $\text{H}_2$  and  $\text{I}_2$  to restore equilibrium.

Again, suppose an equilibrium mixture of gases exists with:

$$k_1[\text{H}_2 \text{ eq}][\text{I}_2 \text{ eq}] = k_2[\text{HI eq}]^2$$

Hydrogen gas is added to the mixture. Rate ( $\longrightarrow$ ) is increased, but Rate ( $\longleftarrow$ ) is unaffected momentarily.

But

$$k_1[\text{H}_2][\text{I}_2] > k_2[\text{HI}]^2$$

$\text{H}_2$  and  $\text{I}_2$  begin decreasing and HI starts increasing until equilibrium is restored. The net effect of adding  $\text{H}_2$  gas is to decrease the concentration of  $\text{I}_2$  and to increase the concentration of HI.

The Mass Law predicts the same result. In an equilibrium mixture of three gases:

$$\frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = K \text{ eq (is 53.9 at 425°C)}$$

If additional HI is added:

$$\frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} > K_{\text{eq}}$$

HI must be partially converted to  $\text{H}_2$  and  $\text{I}_2$ , reducing its concentration and increasing the other two until  $K_{\text{eq}}$  is obtained. The net result of adding additional HI was an increase in  $\text{H}_2$  and  $\text{I}_2$ .

If additional  $\text{I}_2$  vapor is added:

$$\frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} > K_{\text{eq}}$$

$\text{H}_2$  and  $\text{I}_2$  must be partially converted to HI until  $K_{\text{eq}}$  is obtained. The net effect is an increase in [HI] and a decrease in  $[\text{H}_2]$ .

Finally, applying Le Chatelier's principle, when HI gas is added to an equilibrium mixture of the three gases, a "stress" is applied to the [HI]. The only relief that can be obtained results from a decomposition of HI. This the system tends to do. The net result is an increase in  $[\text{H}_2]$  and  $[\text{I}_2]$ . Following the same reasoning, one can determine the effect of adding any of the three gases on the concentrations of an equilibrium mixture.

#### G. EFFECT OF CATALYSIS AND STATE OF SUBDIVISION ON EQUILIBRIUM CONCENTRATIONS

A catalyst always increases the rate of reaction. In the hydrogenation of oils, the platinum surface holds hydrogen atoms firmly in position for collision and addition to the oil. But this is a two-way situation. Just as the platinum holds the hydrogen to be accepted by the oil more easily, it receives it back from the oil just as easily. Both the forward and the reverse reactions are aided. It has been found that a catalyst increases the rate of both forward and reverse reactions equally. The presence of a catalyst does not change equilibrium concentrations.

The effect of the state of subdivision on the rate of reactions is exemplified by the platinum catalyzed reaction. Because the hydrogenation reaction occurs on the platinum surface a large surface area, the catalyst should be finely subdivided. The finer the platinum particles, the greater the area. Again the reverse reaction is benefited as greatly as the forward reaction by the increased area, and the equilibrium concentrations remain unchanged.

#### H. CALCULATIONS USING THE MASS LAW

Not only is the Mass Law Equation useful in telling qualitatively how addition of a reactant will "shift" the equilibrium concentrations, but it may be used to determine one or two of the actual concentrations when the others are known and also to give a quantitative measure of the "shift" in equilibrium concentrations. Two sample calculations appear below:

**EXAMPLE 1.** 5.0 g of hydrogen iodide gas is placed in a 2.5 liter flask at 425°C. What will be the concentration of the three gases when equilibrium is attained?

**SOLUTION:** The initial concentration of HI is:

$$\frac{5.0 \text{ g}}{2.5 \text{ L}} \times \frac{1}{128 \text{ g/mole}} = 0.0156 \text{ mole/liter}$$

Let  $X = [\text{H}_2 \text{ eq}] =$  the equilibrium concentration of  $\text{H}_2$   
 then  $X = [\text{I}_2 \text{ eq}] =$  the equilibrium concentration of  $\text{I}_2$  vapor  
 and  $0.0156 - 2X =$  the equilibrium concentration of HI



In the Mass Law Equation;

$$\frac{[\text{HI eq}]^2}{[\text{H}_2 \text{ eq}][\text{I}_2 \text{ eq}]} = \frac{(0.0156 - 2X)^2}{X^2} = 53.9$$

$$\frac{0.0156 - 2X}{X} = (53.9)^{1/2} = \sqrt{53.9}$$

$$X = 0.00167$$

and the equilibrium concentrations are:

$$[\text{H}_2 \text{ eq}] = [\text{I}_2 \text{ eq}] = 1.67 \times 10^{-3} \text{ mole/liter}$$

**EXAMPLE 2.** 0.05 g of hydrogen gas is added to the 2.5 liter flask in Example 1, and the contents are allowed to return to equilibrium conditions. What is the concentration of iodine vapor?

**SOLUTION:**

$$\text{Let } X = [\text{I}_2]$$

$$\text{then } [\text{HI}] = (0.0156 - 2X) \text{ mole/liter}$$

$$\text{and } [\text{H}_2] = \frac{0.05 \text{ g}}{2 \text{ g/mole}} \times \frac{1}{2.5 \text{ liters}} + X = (0.01 + X) \text{ mole/liter}$$

Substituting in the Mass Law Equation:

$$\frac{(0.0156 - 2X)^2}{(0.01 + X)X} = 53.9$$

Solving the quadratic equation:

$$X = 4.5 \times 10^{-4} \text{ mole/liter} = [\text{I}_2]$$

Notice that the addition of 0.01 mole/liter of  $\text{H}_2$  reduced the equilibrium concentration of  $\text{I}_2$  from  $1.67 \times 10^{-3}$  mole/liter to  $4.52 \times 10^{-4}$  mole/liter. These two calculations are sufficient here. Other similar calculations will be made in discussing weak electrolytes. Notice that the notation eq often is



omitted in the writing of the Mass Law Expression. It appears as follows for the reaction studied:

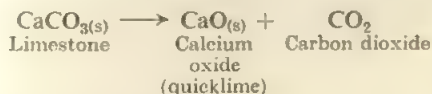
$$\frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = K$$

Nevertheless, the law is valid only when the concentrations are those of a system in equilibrium.

### 3. APPLICATION OF THE PRINCIPLES OF RATES AND EQUILIBRIUM TO CHEMICAL PROCESSES

A number of processes using catalysts have been described and many more could be noted. The role of the catalyst is often not understood, but it is apparent that many processes would be impossible and many would be much more expensive without catalysts. The value of a large surface area was discussed in relation to explosions, or uncontrolled reactions. It is of more value in controlled reactions, chemical processes, some of which will be mentioned later in the text. In many processes, solids are finely powdered and liquids are stirred violently to increase the area and velocity of reaction.

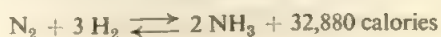
Temperature is often varied to control the rate of reaction. This has been discussed in relation to cooking. It might also be varied to increase the equilibrium percentage of a desired product. One simple commercial process, the calcining of lime to produce quicklime, employs both temperature and concentration factors:



The reaction takes place in a limekiln, a chimney-like furnace, by a blast of hot gases from the bottom (Fig. 22.5). The reaction occurs at about 850°C in the gases as they move up through the continuously descending limestone in the kiln.

High temperature is necessary to raise the equilibrium pressure of the escaping gas to a sufficiently high pressure or concentration. But notice on the decomposition pressure curve (Fig. 22.6) that the decomposition pressure is 760 mm at 912°C. The temperature must be kept lower to prevent the melting of silicates present. This is accomplished at 850°C, where the equilibrium pressure is less than 1 atmosphere in the blast of gases. The escaping CO<sub>2</sub> mixes with the gases so that its partial pressure is much less than atmospheric pressure and the limestone is decomposed rapidly.

A careful choice of reaction conditions is used in the Haber process in which a nitrogen and hydrogen mixture is passed over a specially prepared iron catalyst at 500°C and 1000 atmospheres to produce ammonia. The equation for the reaction is:



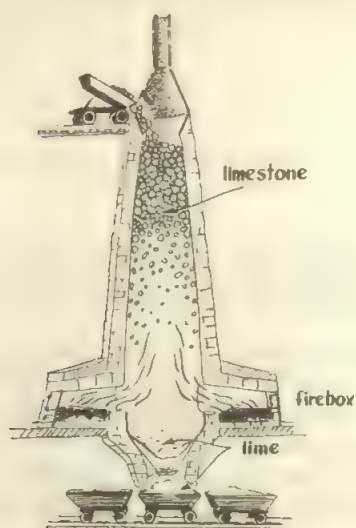


Figure 22.5. Limekiln.

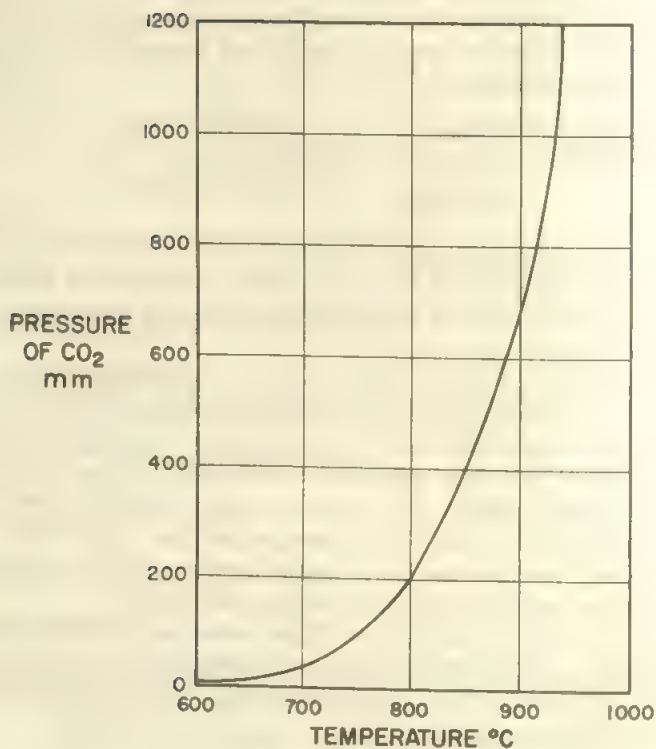


Figure 22.6. Decomposition pressure curve for limestone.

The special conditions are higher temperature, high pressure and a catalyst. The catalyst's only role is to increase the rate of reaction, the rate of approach to equilibrium.

The high pressure results in a high concentration of reactants initially and a high concentration of both products and reactants at and near equilibrium. The high concentration of reactants increases the rate of reaction. The effect on equilibrium concentrations is more subtle, but it can be understood by considering the Mass Law Equation for the reaction:

The Mass Law Expression for the reaction:



is:

$$\frac{[\text{NH}_3 \text{ eq}]^2}{[\text{N}_2 \text{ eq}][\text{H}_2 \text{ eq}]^3} = K \text{ eq}$$

(By convention, the concentrations of products appear in the numerator; the concentration of reactants in the denominator. Each concentration is raised to the power of its coefficient in the balanced equation.)

Now consider a mixture of the three gases at equilibrium in *situation 1*. All the concentrations will be equilibrium concentrations and:

$$\frac{[\text{NH}_3]_1^2}{[\text{N}_2]_1[\text{H}_2]_1^3} = K \text{ eq} \quad (\text{Where the subnumber indicates concentrations in situation 1.})$$

Now, suppose, by moving a piston, the gases are compressed into one-half the volume. Instantaneously all concentrations in the container are doubled. At that instant

$$\frac{[\text{NH}_3]_2^2}{[\text{N}_2]_2[\text{H}_2]_2^3} \neq K \text{ eq}$$

but because

$$[\text{NH}_3]_2 = 2[\text{NH}_3]_1, \quad [\text{N}_2]_2 = 2[\text{N}_2]_1 \quad \text{and} \quad [\text{H}_2]_2 = 2[\text{H}_2]_1,$$

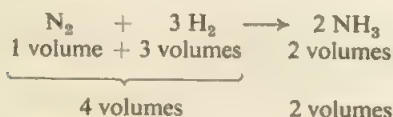
$$\frac{(2[\text{NH}_3]_1)^2}{(2[\text{N}_2]_1)(2[\text{H}_2]_1)^3} = \frac{2^2}{2 \times 2^3} \times K \text{ eq} = 1/4 K \text{ eq}$$

To restore the equilibrium constant, some  $\text{N}_2$  and  $\text{H}_2$  will combine, reducing the value of the denominator and forming some  $\text{NH}_3$ , which increases the value of the numerator. The net effect of an increase in pressure has been an increase in the concentration and per cent of ammonia produced at equilibrium, coupled with the aforementioned increase in rate. Table 22.1 shows the percentage of a nitrogen and hydrogen mixture (in 1 to 3 ratio) converted to ammonia at  $500^\circ\text{C}$  and various pressures. The results agree with the discussion. Application of Le Chatelier's Principle would also predict the increase in ammonia percentage with high pressure. A sudden decrease in

Table 22.1. Per cent Ammonia at Equilibrium at 500 C

<i>Pressure Atm.</i>	<i>% NH<sub>3</sub></i>
50	5.56
100	10.61
300	26.44
600	42.15
1000	57.47

volume places a stress on pressure; the system must rearrange itself in a tendency to reduce the pressure. It can by 4 volumes going to 2 volumes:



The result is a decrease in  $\text{N}_2$  and  $\text{H}_2$  concentrations and an increase in the concentration of  $\text{NH}_3$ .

High temperature does not favor a high equilibrium concentration of ammonia. The reaction producing ammonia is exothermic. The reverse, the endothermic reaction, is favored. This is shown in Table 22.2 in which the per cent conversion of  $\text{N}_2$  and  $\text{H}_2$  in 1 to 3 mixtures at 1000 atm is recorded for several temperatures.

Table 22.2. Per cent Conversion to Ammonia at 1000 atm.

<i>Temp. °C</i>	<i>% NH<sub>3</sub></i>
300	92
400	80
500	57
600	31
700	13

At a temperature of 500°C, a maximum of 57 per cent  $\text{N}_2$  and  $\text{H}_2$  can be converted to  $\text{NH}_3$ . At 400°C, 80 per cent could be converted. However, the time required at 400°C is much greater than that needed to get the 57 per cent possible at 500°C. In practice the gases are passed over the catalyst at such a rate that equilibrium is not reached; only about 40 per cent ammonia is gained. The gases are either cooled to liquefy the ammonia or are bubbled through water to "strip" the ammonia. The unreacted elemental gases are



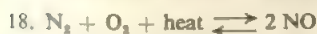
passed over the catalyst with the next mixture of gases. By this recycling procedure, substantially all the nitrogen and hydrogen are converted to ammonia.

### EXERCISES

- State two reasons why 100% of the reactants are not converted to products in a chemical reaction.
- Why is time significant in chemical reactions carried out at elevated temperatures?
- Define:
 

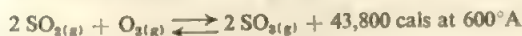
a. rate of reaction	e. chemical equilibrium
b. catalyst	f. equilibrium constant
c. exothermic	g. activation energy
d. reversible reaction	
- What methods might be used to measure the rate of a reaction?
- What is a general rule relating a rise in temperature to the rate of increase in a reaction rate?
- Name four instances in which the temperature is controlled to control the rate of a chemical reaction.
- Why should a chemical reaction proceed twice as fast with a 10° rise in temperature?
- Will all exothermic reactions proceed at room temperature?
- Explain why the reaction of  $H_2$  and  $I_2$  gas has an activation energy.
- What is  $k_1$  in the equation:  

$$\text{Rate} = k_1[A][B]?$$
- What does this mean:  $[NH_3]$ ?
- Explain why an empty gasoline can will explode when lighted with a match, whereas a burning match is extinguished when dropped into gasoline?
- Describe two ways that catalysts may take part in a chemical reaction.
- How might one determine that a mixture of gases is at chemical equilibrium?
- Does changing the temperature ever change the value of the equilibrium constant? Explain.
- Does changing the pressure change the value of the equilibrium constant?
- Does a catalyst change the value of the equilibrium constant?



The equation above is for an endothermic reversible reaction. What happens to the nitric oxide concentration in an equilibrium mixture of the gases when the temperature is raised?

- Explain why a catalyst, high pressure, and high temperature are used for the Haber process.
- State Le Chatelier's Principle.
- Use Le Chatelier's Principle to show how the equilibrium pressure of ammonia (in a mixture with hydrogen and nitrogen) varies with both temperature and pressure.
- The important reaction of the contact process is represented by the equation below:



- Will one obtain a greater percentage of  $SO_3$  at  $650^\circ C$ ?
  - Will one obtain a greater percentage of  $SO_3$  at high pressure?
- Explain each answer using Le Chatelier's Principle.
- Write the equilibrium constant expression for each of the following reactions.
    - $C_2H_6(g) \longrightarrow C_2H_4(g) + H_2(g)$
    - $2 NO(g) + O_2(g) \longrightarrow 2 NO_2(g)$
    - $NO_2(g) + SO_2(g) \longrightarrow SO_3(g) + NO(g)$
    - $3 O_2(g) \longrightarrow 2 O_3(g)$

## PROBLEMS

1. Using data from Table 22.1, calculate the equilibrium constant for the reaction occurring in the Haber process at 500°C.
2. Calculate the constant at 300°C. (See Table 22.2.)
3. Calculate the concentration of hydrogen iodide in moles per liter if the reaction vessel (p. 332) had been reduced in volume to 0.5 liter at 425°C. Use  $K_{eq} = 54$  at 425°C.

## IONIC EQUILIBRIA

Many chemical reactions take place in water solutions. Soil chemistry is water solution chemistry. Tree sap and other plant fluids are water solutions. The fluid base of blood is water. Gastric juices that decompose food stuff in the stomach are water solutions. In most reactions occurring in the biosphere, the living shell around the earth, water is present and plays an important role.

Many industrial processes involve water solutions. The treatment of wood pulp, the dissolving of silver from its ore and the preparation and action of fertilizers are a few in which solutions play a leading role.

In all these natural and industrial processes and in most reactions in which water takes part, ions are involved. In many the ionic concentrations are maintained at a very low level but are very important. There is only about 0.01 mole of hydronium ion per liter of stomach fluid but that acid concentration is sufficient to digest food. Were the solution more concentrated in the acid ion, the stomach lining would dissolve. Soil solutions must contain some iron in solution. The amount is described as parts per million, but without this concentration the plant leaves turn yellow, a condition called chlorosis.

These are but two examples of the critical importance of ions and ionic concentrations. These concentrations are set and controlled by chemical equilibria that in many ways are similar to those discussed in the previous chapter. To understand the processes above or to devise others one must understand ionic equilibria.

This chapter is divided into four sections; each section is concerned with equilibria involving ions. Section 1 discusses homogeneous reactions, reactions in which all molecules and ions participating are in one phase, that phase being a water solution. Ionization characterizes the reactions, the

ionization of weak electrolyte acids and bases. Section 2 is a study of homogeneous equilibria of soluble strong electrolytes: weak acids and bases and complex ions. Section 3 is a study of heterogeneous equilibria: a study of dissociation in the dissolving of salts and the dissolving of metals in solution. Section 4 is an introduction to systems in which more than one equilibrium is involved.

## 1. HOMOGENEOUS EQUILIBRIA OF WEAK ELECTROLYTES

### A. WEAK ELECTROLYTES

Weak electrolytes were considered in Chapter 17. They are pure substances:

- (1) whose solutions freeze at a slightly lower temperature, boil at a slightly higher temperature and exhibit a slightly greater osmotic pressure than do solutions of non-electrolytes of the same concentration.
- (2) whose solutions conduct an electric current, but are poor conductors.
- (3) that are written as molecules in an ionic equation.
- (4) that are formed, and whose formation is the motive force in certain ionic reactions.

Weak electrolytes may be contrasted with strong electrolytes. They are pure substances:

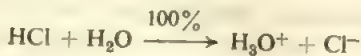
- (1) whose solutions lower the freezing point, raise the boiling point and have an osmotic pressure two, three or four times greater than a solution of a non-electrolyte of the same concentration.
- (2) whose solutions are excellent electrolytic conductors.
- (3) that are written as ions in an ionic equation (when in solution).
- (4) whose formation may be the motive force of a reaction only when insoluble in water.

Further understanding of weak electrolytes might best be obtained by a more detailed comparison with strong electrolytes.

### B. pH

Before discussing weak electrolytes, which, whether they are acids or bases, are concerned with hydronium ion concentration, an alternate and much used method for indicating the hydronium ion concentration should be discussed. In natural systems—soils, plant fluids and animal fluids—the hydronium ion concentration varies well within the limits of  $1 \text{ M H}_3\text{O}^+$  and  $1 \times 10^{-14} \text{ M H}_3\text{O}^+$ .

Consider the hydronium ion concentrations of solutions of hydrochloric acid. Hydrochloric acid is a strong electrolyte and is completely ionized in water.



The concentration of non-ionized HCl in  $1 \text{ M HCl}$  is zero; of  $\text{H}_3\text{O}^+$  is  $1 \text{ M}$ ,



and of  $\text{Cl}^-$  is 1 M. Table 23.1 lists the  $\text{H}_3\text{O}^+$  concentrations in moles per liter of various HCl solutions.

Table 23.1.

<i>Molarity of HCl</i>	$[\text{H}_3\text{O}^+]$	<i>Molarity of HCl</i>	$[\text{H}_3\text{O}^+]$
0.1 M HCl	$0.1 \times 10^{-1}$	0.004 M HCl	$4 \times 10^{-3}$
0.02 M HCl	$2 \times 10^{-2}$	0.001 M HCl	$1 \times 10^{-3}$
0.01 M HCl	$1 \times 10^{-2}$	0.0006 M HCl	$6 \times 10^{-4}$

To avoid using very small fractions in indicating hydronium ion concentrations, the chemist invented a term called pH with the relationship to  $[\text{H}_3\text{O}^+]$  as shown below:

1 M  $\text{H}_3\text{O}^+$  has a pH of 0  
 0.1 M  $\text{H}_3\text{O}^+$  has a pH of 1  
 0.01 M  $\text{H}_3\text{O}^+$  has a pH of 2  
 0.001 M  $\text{H}_3\text{O}^+$  has a pH of 3  
 0.0001 M  $\text{H}_3\text{O}^+$  has a pH of 4

The pH of a solution increases in magnitude as the acidity decreases. When the acidity  $[\text{H}_3\text{O}^+]$  changes by a factor of 10, the pH changes by 1.

The pH is related to the logarithm of the hydronium ion concentration:

$$\begin{aligned} 0.01 &= 1/100 = 1/10^2 = 10^{-2} \quad (-2 \text{ is the log of } 0.01) \\ 0.0001 &= 1/10000 = 1/10^4 = 10^{-4} \quad (-4 \text{ is the log of } 0.0001) \end{aligned}$$

The pH is defined by this equation:

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

and may be applied as follows:

EXAMPLE 1. Find the pH of 0.001 M HCl

SOLUTION: The  $[\text{H}_3\text{O}^+]$  of 0.001 M HCl is 0.001

$$\begin{aligned} \log [\text{H}_3\text{O}^+] &= \log 0.001 = -3 \\ \text{pH} &= -\log [\text{H}_3\text{O}^+] = -\log 0.001 = 3 \end{aligned}$$

EXAMPLE 2. Find the pH of 0.003 M HCl

SOLUTION: The pH of 0.01 M HCl is:

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log 0.01 = -(-2) = 2$$

The pH of 0.001 M HCl is:

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log 0.001 = -(-3) = 3$$

0.003 M  $\text{H}_3\text{O}^+$  lies between 0.01 M  $\text{H}_3\text{O}^+$  and 0.001 M  $\text{H}_3\text{O}^+$ . The pH will be greater than 2 and less than 3. It happens that 0.003 may be written  $10^{-2.523}$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log 10^{-2.523} = -(-2.523) = 2.523$$

One senses that the pH of 0.003 M HCl (2.523) is intermediate between the pH of 0.01 M HCl (2) and the pH of 0.001 M HCl (3), but may not know the exact value without access to a table of logarithms or a slide rule. A table showing logs of two figure numbers is reproduced here (Table 23.2).

**Table 23.2. Table of Logarithms**

	.0	.1	.2	.3	.4	.5	.6	.7	.8	.9
1	000	041	079	114	146	176	204	230	255	279
2	301	322	342	362	380	398	415	431	447	462
3	477	491	505	519	532	544	556	568	580	591
4	602	613	623	634	644	653	663	672	681	690
5	699	708	716	724	732	740	748	756	763	771
6	778	785	792	799	806	813	820	826	833	839
7	845	851	857	863	869	875	881	887	892	898
8	903	909	914	919	924	929	935	940	945	949
9	954	959	964	969	973	978	982	987	991	996

To determine the logarithm of a number, first write it in the correct exponential form:

$$0.0042 = 4.2 \times 10^{-3}$$

Find the logs of the two parts and add. The fractional logs, logs for numbers between 1 and 10, are positive and must be read off the table.

Log 4.2 is found in the table as follows:

	.0	.1	.2	.3	.4	.5	.6	.7	.8	.9
1										
2										
3										
4			0.623							
5										
6										
7										
8										
9										

$$\begin{array}{r}
 \text{Log } 4.2 \times 10^{-3} = +0.623 + (-3) \\
 \quad -3.000 \\
 \quad +0.623 \\
 \hline
 \quad -2.377
 \end{array}$$

The pH of a 0.0042 M HCl is then

$$\begin{aligned}\text{pH} &= -\log [\text{H}_3\text{O}^+] = -\log (4.2 \times 10^{-3}) = -(0.623 - 3.000) \\ &= -(-2.377) = 2.377\end{aligned}$$

### C. WEAK ACIDS

Hydrochloric acid is a strong acid. It is completely ionized in water:

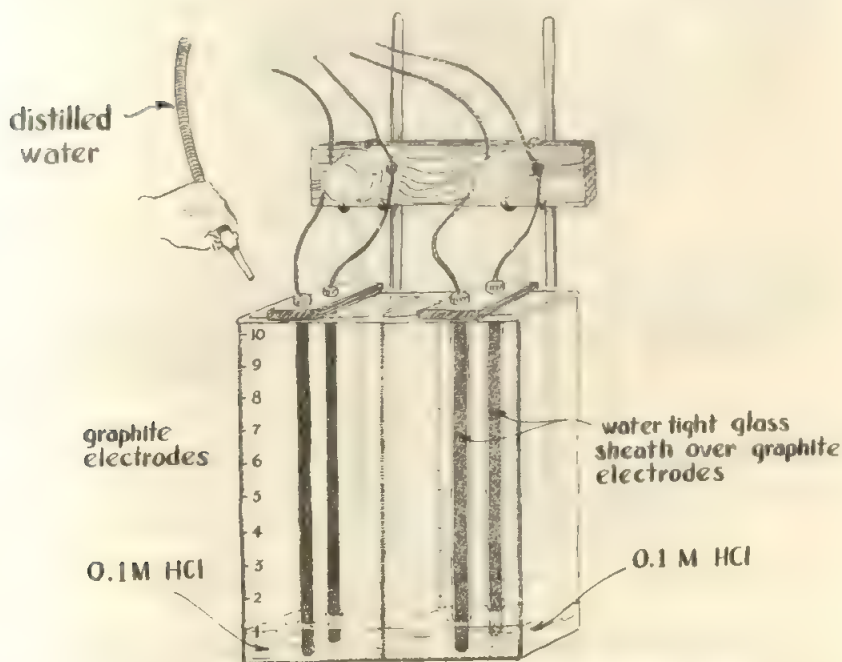
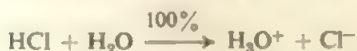


Figure 23.1. A study of the degree of ionization of HCl.

This fact, assumed in the discussion of pH, may be shown with an experiment on conductivity.

**Experiment 1.** A 0.10 M HCl solution is added to both compartments of a divided glass battery jar (Fig. 23.1) containing two pairs of graphite electrodes. When immersed in a conducting solution, each pair of electrodes completes a circuit through a light bulb. Each pair of electrodes reaches the bottom of the jar. The pair on the left is uncovered the whole depth of the container whereas the pair on the right is covered tightly down to 1 cm from the bottom. In effect these electrodes are 1 cm in height. The 0.10 M HCl is added to the depth of 1 cm in each cell, covering each pair of electrodes to that depth. The exposed section of the electrodes on the right is completely

covered. The two light bulbs glow with equal intensity. Distilled water is now added to the compartment on the left. As the incoming water mixes and the solution level rises, the bulb on the left retains its intensity.

The explanation is simple. The 0.1 molar hydrochloric acid was completely ionized. Dilution did not change the number of ions. The same number of conducting ions remained between the electrodes, and the intensity of light did not change. Upon addition of distilled water to the compartment

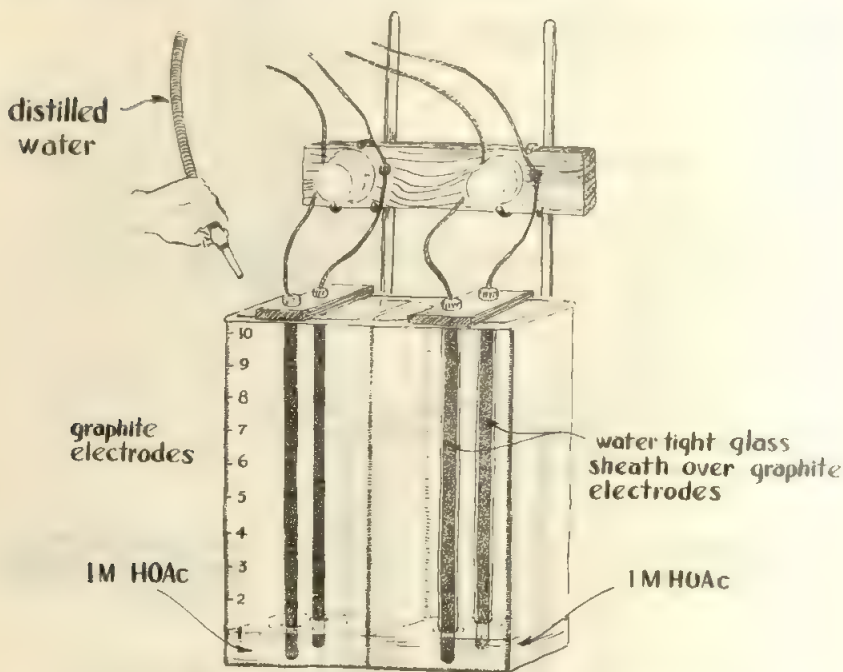


Figure 23.2. A study of the degree of ionization of acetic acid.

ment on the right (not shown in the figure), the light dimmed considerably, because though the same number of ions existed in solution, fewer lay in the 1 cm layer between the 1 cm electrodes.

**Experiment 2.** After pouring out the hydrochloric acid solutions and washing and drying the battery jar, 1 molar acetic acid is added to each compartment to the height of 1 cm (Fig. 23.2). Although the molar concentration of this solution is 10 times that of the 0.1 M HCl previously in the jar, the light bulbs glow much less brightly than before. This is because acetic acid is a weak electrolyte and is only partially ionized in water. Additional evidence of this fact is obtained by adding distilled water in the compartment on the left. As the water is added, the light becomes brighter and brighter. Apparently, the addition of water to the left compartment has created more ions. If more hydronium and acetate ions were formed by dilution (adding water), acetic acid is not 100% ionized in a 1 molar solution.



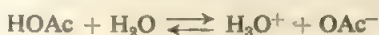
The increase in the number of ions can be measured quantitatively by removing solution from the left hand compartment until the light bulbs glow with the same intensity. This happens when the more dilute solution (now 0.1 M HOAc) is removed to a height of 3.1 cm. It follows that the number of ions were increased by

$$\frac{10}{3.1} = 3.2 \text{ times}$$

with the tenfold dilution.

When distilled water is added to the compartment on the right, the light dims, but not so rapidly as with the solution of hydrochloric acid. More than one-tenth the *original* number of ions are in the 1 cm layer between the 1 cm electrodes when the diluted solution stands 10 cm in the cell.

The fact that any solution of acetic acid will produce more  $\text{H}_3\text{O}^+$  and  $\text{OAc}^-$  ions when diluted, plus the fact that 1.0 M HOAc has the same capacity to neutralize a base as does 1.0 M HCl, indicates that the small percentage of ionization of acetic acid is governed by an equilibrium reaction.



It appears that the equilibrium is dynamic, that the forward and reverse rates are dependent upon concentrations, that the rates change with changing concentrations upon dilution and, therefore, change the percentage ionized at equilibrium.

#### D. DERIVATION OF $K_a$

A consideration of the rate equations will indicate how the ionic concentrations should change with dilution. Pursuing the reasoning of the last chapter, the rate of the forward reaction, ionization of acetic acid:



may be given by this expression:

$$\text{Rate } (\longrightarrow) = k[\text{HOAc}][\text{H}_2\text{O}]$$

where  $k$  is the rate when  $[\text{HOAc}] = [\text{H}_2\text{O}] = 1 \text{ mole/liter}$ .

However, the concentration of water changes by a very small percentage when a weak electrolyte ionizes in it. Water is at a very high concentration. Pure water is about 55.5 M water:

$$\frac{1000 \text{ g/L}}{18 \text{ g/mole}} = 55.5 \text{ moles/L} = 55.5 \text{ M}$$

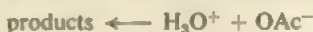
Again, nearly 1000 g of water is added to 60 g of acetic acid to make one liter of 1 M HOAc. The concentration drops to perhaps 55 M. Less than 1 per cent of the acetic acid is ionized at equilibrium, and the concentration

of water decreases negligibly to 54.99 M. Because the concentration of water is essentially constant, the rate equation may become:

$$\text{Rate } (\longrightarrow) = k_1[\text{HOAc}]$$

where  $k_1 = k[\text{H}_2\text{O}]$ , the product of two constants.

The rate equation for the reverse reaction:



is given by:

$$\text{Rate } (\longleftarrow) = k_2[\text{H}_3\text{O}^+][\text{OAc}^-]$$

At equilibrium,  $\text{Rate } (\longrightarrow) = \text{Rate } (\longleftarrow)$

$$k_1[\text{HOAc eq}] = k_2[\text{H}_3\text{O}^+ \text{eq}][\text{OAc}^- \text{eq}]$$

In this reaction,  $k_2$  is much greater than  $k_1$  and only very low concentrations of  $\text{H}_3\text{O}^+$  and  $\text{OAc}^-$  are required to make the rates equal. (This will be shown experimentally later.) Suppose now that to a 100 ml sample of 1 M HOAc, in which the equilibrium concentration of  $\text{H}_3\text{O}^+$  and  $\text{OAc}^-$  and undissociated HOAc exists, one adds an additional 100 ml of water. All participating concentrations (except that of water, which does not appear in the rate equations) are one-half the initial value.

$\text{Rate } (\longrightarrow)$  will have been "halved"  $= k_1 \times 1/2 \times [\text{HOAc}]$

$\text{Rate } (\longleftarrow)$  will have been reduced to  $1/4$

$$= 1/2[\text{H}_3\text{O}^+] \times 1/2[\text{OAc}^-]$$

$$\text{Rate } (\longrightarrow) = 2 \text{Rate } (\longleftarrow)$$

and  $\text{H}_3\text{O}^+$  ions are being formed faster than they are being consumed. This inequality in rate persists until the ionic concentrations become great enough and the HOAc concentration small enough to restore equilibrium. Dilution increased the total number of ions, although the number of ions in 100 ml was decreased. To repeat, in 200 ml of 0.5 M HOAc there are more ions than in 100 ml of 1.0 M HOAc, but fewer ions are present in 100 ml of 0.5 M HOAc than in 100 ml of 1.0 M HOAc.

Rearrangement of the equated rate expressions gives the Mass Law Expression:

$$K_a = \frac{k_1}{k_2} = \frac{[\text{H}_3\text{O}^+ \text{eq}][\text{OAc}^- \text{eq}]}{[\text{HOAc eq}]}$$

$K_a$  is the equilibrium constant for the ionization of a weak acid. From this equation, it is readily apparent that a simultaneous, proportionate reduction in all three concentrations would cause the expression to be less than  $K_a$  until some of the HOAc ionized to decrease the denominator and increase the numerator.

E. EVALUATION OF  $K_a$ 

In the deriving of the equilibrium constant expression, one merely shows that if rates depend on concentrations as they appear to, at equilibrium this expression:

$$\frac{[\text{H}_3\text{O}^+][\text{OAc}^-]^*}{[\text{HOAc}]}$$

is equal to a number (at a certain temperature). One cannot use the equation quantitatively until the number has been determined using experimental data

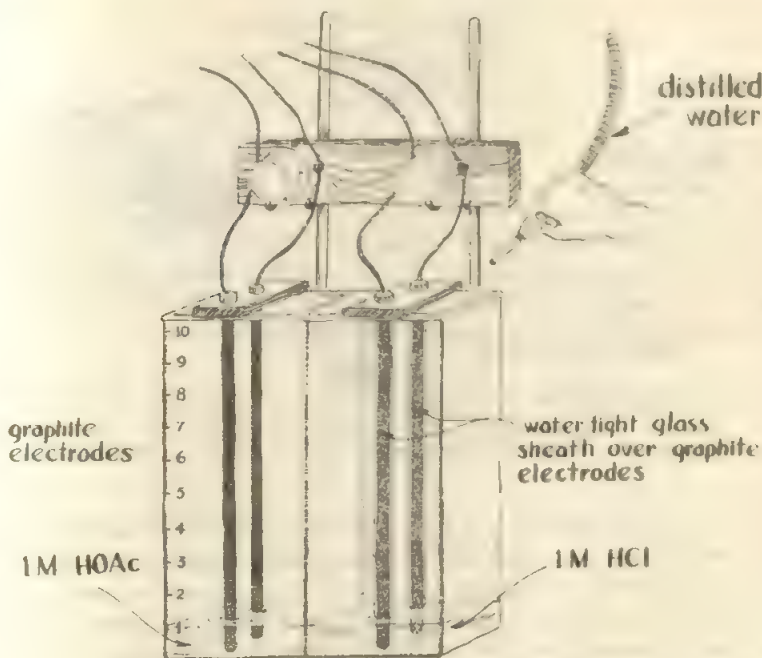


Figure 23.3. Determination of the  $[\text{H}_3\text{O}^+]$  of 1.0 M HOAc.

An experiment may be performed using the apparatus (Fig. 23.3) to determine the value of  $K_a$  at room temperature.

**Experiment 3.** A 1.0 M HOAc solution is added to the left compartment until the electrode is covered to the height of 1 cm. A 1.0 M HCl solution is added to the right compartment to the same height and just covering the 1 cm electrodes. The light on the right glows much more brightly than the one on the left, because more ions are present.

Distilled water is added with stirring to the HCl in the compartment on the right until it stands at the 10 cm mark. During the addition the light grew dimmer, but was still brighter than the light on the left. The solution is then siphoned from the same compartment down to the 1 cm level. The light

\* The notation "eq" will be dropped for the balance of the chapter.

intensity remained the same, because the layer of solution between the electrodes was not disturbed.

The HCl solution in the right hand compartment is diluted the second time with distilled water to the 10 cm mark. The light intensity is still greater than that on the left. Again the solution is siphoned down to the 1 cm level, and again distilled water is added slowly, because the light on the right is not much brighter than the light on the left.

When the height of the dilute HCl solution rises to 2.5 cm both lights glow with the same intensity. It may be assumed that the same number of ions lay

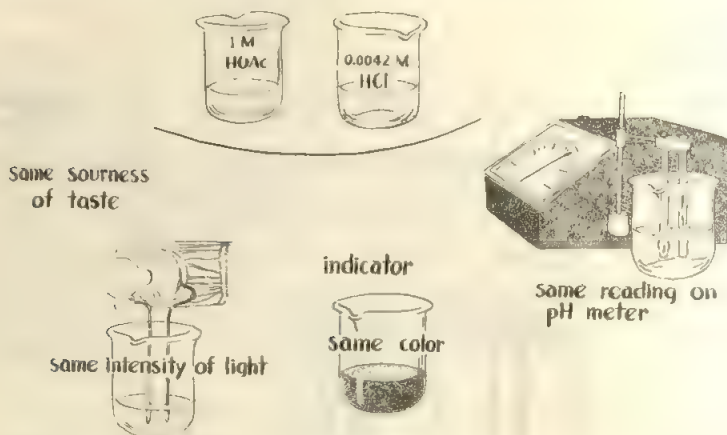


Figure 23.4. The similarities between 0.0042 M HCl and 1.0 M HOAc.

between the 1 cm electrodes in the two vessels. This is not exactly true, for  $\text{H}_3\text{O}^+$  and  $\text{OAc}^-$  ions are present in the left hand container, while  $\text{H}_3\text{O}^+$  and  $\text{Cl}^-$  ions are present in the right. Unless the  $\text{Cl}^-$  ion conducts equally as well as the  $\text{OAc}^-$  ion, the ionic concentrations need not be the same. However, the light hydronium ion carries a great share of the current, making the difference between the conductivity of  $\text{OAc}^-$  and  $\text{Cl}^-$  negligible.

The final HCl solution has a concentration of:

$$1.0 \text{ mole/liter} \times \frac{1}{10} \times \frac{1}{10} \times \frac{1}{2.5} = 0.0040 \text{ mole/liter}$$

(first, second and third dilutions)

Because all the HCl is ionized, the concentration of  $\text{H}_3\text{O}^+$  and  $\text{Cl}^-$  in the HCl solution is 0.0040 M. It follows that the  $\text{H}_3\text{O}^+$  and  $\text{OAc}^-$  concentrations in 1 M HOAc are 0.0040 M.

This is not the only method for determining the concentration of hydronium ions in 1.0 M HOAc. Figure 23.4 indicates that 0.0042 M HCl and 1.0 M HOAc have:

- (1) the same sourness of taste.
- (2) the same conductivity.



- (3) the same color in indicator solutions.
- (4) the same reading on a pH meter, which measures precisely the hydronium concentration by its effect on the voltage of a certain primary cell.

To complete the determination of  $K_a$ :

the  $[H_3O^+] = 0.0042$  mole/liter (measured)

the  $[OAc^-] = 0.0042$  mole/liter (appears ion for ion with  $H_3O^+$ )

and the non-ionized HOAc concentration:

$$[HOAc] = 1 - 0.0042 \text{ mole/liter} = 0.996 \text{ mole/liter}$$

Substituting these values in the equation, one obtains:

$$K_a = \frac{[H_3O^+][OAc^-]}{[HOAc]} = \frac{0.0042 \times 0.0042}{0.996} = 1.75 \times 10^{-5}$$

Using only significant figures,  $K_a = 1.8 \times 10^{-5}$ ; one might as well have used 1 mole/liter for HOAc as 0.996 mole/liter.

The value of the ionization constant ( $K_a$ ) may be determined using solutions of acetic acid of concentrations other than 1.0 M. One need merely find the hydronium ion concentration in another acetic acid solution in a manner discussed for 1.0 M HOAc and substitute in the Mass Law Expression. Table 23.3 shows the measured hydronium ion concentrations for HOAc

**Table 23.3. The  $[H_3O^+]$  and Value of  $K_a$  for Acetic Acid for Solutions of Different Concentrations**

M HOAc	$H_3O^+$	$K_a$
0.100	0.00135	$1.82 \times 10^{-5}$
0.010	0.00042	$1.76 \times 10^{-5}$
0.001	0.000124	$1.75 \times 10^{-5}$

solutions of various molarities, with the value of the ionization constant calculated using those values. One can see that the values of the ionization constant calculated at different concentrations are nearly the same and are close to  $1.8 \times 10^{-5}$ .

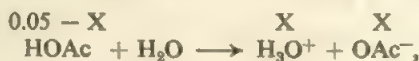
#### F. CALCULATION OF THE $H_3O^+$ CONCENTRATION IN SOLUTIONS OF WEAK ACIDS

Once the equilibrium constant  $K_a$  has been calculated, one can use the constant expression to calculate the  $H_3O^+$  concentration of solutions of other concentrations.

EXAMPLE 4. What is the hydronium ion concentration of 0.05 M HOAc at room temperature?  $K_a = 1.8 \times 10^{-5}$

SOLUTION: Let  $X = [H_3O^+]$

And since  $H_3O^+$  was produced only by this equation



$$[\text{OAc}^-] = X$$

$$\text{and } [\text{HOAc}] = 0.05 - X$$

Then

$$\frac{[H_3O^+][\text{OAc}^-]}{[\text{HOAc}]} = \frac{X^2}{0.05 - X} = 1.8 \times 10^{-5}$$

One may solve the quadratic equation:

$$X^2 = (0.05 - X)(1.8 \times 10^{-5})$$

$$X^2 + 1.8 \times 10^{-5} X - 9 \times 10^{-7} = 0$$

$$X = \frac{-1.8 \times 10^{-5} \pm \sqrt{(1.8 \times 10^{-5})^2 + 4 \times 9 \times 10^{-7}}}{2}$$

$$= \frac{-1.8 \times 10^{-5} \pm 1.9 \times 10^{-3}}{2}$$

$$= 9.4 \times 10^{-4} \text{ moles/liter}$$

or one may assume that  $X$  is very small and that  $0.05 - X \approx 0.05$

$$\frac{X^2}{0.05} = 1.8 \times 10^{-5}$$

$$X^2 = 9.0 \times 10^{-8}$$

$$X = 9.5 \times 10^{-4} \text{ moles/liter}$$

In this case 0.05 could be assumed equal to  $0.05 - X$  without a great error, for  $X = 9.5 \times 10^{-4}$ .  $0.05 - X = 0.04905$ , but the answers are significant to only two figures. When the equilibrium constant is  $5 \times 10^{-4}$  or smaller, the  $X$  may be neglected without serious error.

According to the calculations:

$$[H_3O^+] = 9.4 \times 10^{-4} \text{ mole/liter}$$

$$[\text{OAc}^-] = 9.4 \times 10^{-4} \text{ mole/liter}$$

$$\text{and } [\text{HOAc}] = \text{a bit less than } 0.05 \text{ mole/liter}$$

The pH may be calculated:

$$\text{pH} = 4.000 - \log 9.4 = 4.000 - 0.973 = 3.027$$

\*  $\approx$  means approximately equal to.

**EXAMPLE 5.** Calculate the hydronium ion concentration and pH of a solution containing 1 mole of HOAc and 0.6 mole of NaOAc (sodium acetate) per liter.  $K_a = 1.8 \times 10^{-5}$ .

**SOLUTION:** NaOAc, a strong electrolyte, is completely ionized in solution, and the solution contains 0.6 M  $\text{Na}^+$  and 0.6 M  $\text{OAc}^-$ . The hydronium ion present comes from partial ionization of acetic acid.



$$\text{If } [\text{H}_3\text{O}^+] = X$$

$$[\text{OAc}^-] = 0.6 + X$$

$$[\text{HOAc}] = 1 - X$$

$$[\text{Na}^+] = 0.6 \text{ (but is of no consequence in this problem for it does not appear in the equilibrium expression).}$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{OAc}^-]}{[\text{HOAc}]} = \frac{X(0.6 + X)}{1 - X}$$

$$\text{but } 0.6 + X \approx 0.6$$

$$\text{and } 1 - X \approx 1.0$$

$$\frac{X \times 0.6}{1} = 1.8 \times 10^{-5}$$

$$X = 3 \times 10^{-5} \text{ mole/liter} = [\text{H}_3\text{O}^+]$$

$$\text{pH} = 5.00 - \log 3 = 5.00 - 0.477 = 4.523$$

The addition of the conjugate base ( $\text{OAc}^-$ ) of the acid HOAc suppresses the hydronium ion concentration. This phenomenon is known as the *common ion effect*.

**Table 23.4. Ionization Constants of Weak Acids**

Acid	Reactions	Constant
Acetic	$\text{H}_2\text{O} + \text{CH}_3\text{COOH} \rightarrow \text{H}_3\text{O}^+ + \text{CH}_3\text{COO}^-$	$1.8 \times 10^{-5}$
Benzoic	$\text{H}_2\text{O} + \text{C}_6\text{H}_5\text{COOH} \rightarrow \text{H}_3\text{O}^+ + \text{C}_6\text{H}_5\text{COO}^-$	$6.6 \times 10^{-5}$
Carbonic	$\text{H}_2\text{O} + \text{H}_2\text{CO}_3 \rightarrow \text{H}_3\text{O}^+ + \text{HCO}_3^-$	$4.2 \times 10^{-7}$
Formic	$\text{H}_2\text{O} + \text{HCOOH} \rightarrow \text{H}_3\text{O}^+ + \text{HCOO}^-$	$2.1 \times 10^{-4}$
Hydrocyanic	$\text{H}_2\text{O} + \text{HCN} \rightarrow \text{H}_3\text{O}^+ + \text{CN}^-$	$4.0 \times 10^{-10}$
Hydrofluoric	$\text{H}_2\text{O} + 2 \text{HF} \rightarrow \text{H}_3\text{O}^+ + \text{HF}_2^-$	$6.9 \times 10^{-4}$
Hydrogen sulfide	$\text{H}_2\text{O} + \text{H}_2\text{S} \rightarrow \text{H}_3\text{O}^+ + \text{HS}^-$	$1.0 \times 10^{-7}$
Nitrous	$\text{H}_2\text{O} + \text{HNO}_2 \rightarrow \text{H}_3\text{O}^+ + \text{NO}_2^-$	$4.5 \times 10^{-4}$
Oxalic	$\text{H}_2\text{O} + \text{H}_2\text{C}_2\text{O}_4 \rightarrow \text{H}_3\text{O}^+ + \text{HC}_2\text{O}_4^-$	$3.8 \times 10^{-2}$
Phenol	$\text{H}_2\text{O} + \text{C}_6\text{H}_5\text{OH} \rightarrow \text{H}_3\text{O}^+ + \text{C}_6\text{H}_5\text{O}^-$	$1.0 \times 10^{-10}$
Phosphoric	$\text{H}_2\text{O} + \text{H}_3\text{PO}_4 \rightarrow \text{H}_3\text{O}^+ + \text{H}_2\text{PO}_4^-$	$7.5 \times 10^{-3}$
Propionic	$\text{H}_2\text{O} + \text{C}_2\text{H}_5\text{COOH} \rightarrow \text{H}_3\text{O}^+ + \text{C}_2\text{H}_5\text{COO}^-$	$1.4 \times 10^{-5}$

**EXAMPLE 6.** There are other weak acids besides HOAc. One, benzoic acid (represented as HOBz), has a constant of  $6.6 \times 10^{-5}$ . Find the  $[\text{H}_3\text{O}^+]$  and the pH of 0.02 M HOBz.

## SOLUTION:

$$\text{Let } X = [\text{H}_3\text{O}^+]$$

$$\text{then } [\text{OBz}^-] = X$$

$$\text{and } [\text{HOBz}] = 0.02 - X \approx 0.02$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{OBz}^-]}{[\text{HOBz}]} = \frac{X^2}{0.02} = 6.6 \times 10^{-5}$$

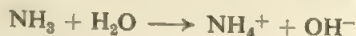
$$X^2 = 1.32 \times 10^{-6}$$

$$X = 1.15 \times 10^{-3} \text{ M H}_3\text{O}^+$$

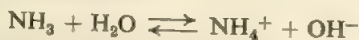
$$\text{pH} = 3.00 - \log 1.15 = 3.00 - 0.060 = 2.94$$

## G. WEAK ELECTROLYTE BASE

The "case of the weak base" parallels the case of the weak acid. A weak base (ammonia solution is the only weak electrolyte base that is of concern) ionizes in water to produce hydroxide ions:



Conductivity experiments comparing solutions of ammonia with solutions of the strong base NaOH show that only a small fraction of the  $\text{NH}_3$  molecules are ionized at one time. The ionization is a reversible reaction and quickly comes to equilibrium:



The rate of ionization at a set temperature is a function of concentration:

$$\text{Rate } (\longrightarrow) = k[\text{NH}_3][\text{H}_2\text{O}]$$

but because  $[\text{H}_2\text{O}]$  changes but little, a simpler equation is used:

$$\text{Rate } (\longrightarrow) = k_1[\text{NH}_3]$$

where  $k_1 = k[\text{H}_2\text{O}]$ . (The  $k$ 's in these rate equations have a different magnitude than those for other reversible reactions.)

The reverse rate, the rate of recombination of ions, is a function of the ionic concentrations:

$$\text{Rate } (\longleftarrow) = k_2[\text{NH}_4^+][\text{OH}^-]$$

At equilibrium the concentrations have adjusted themselves so that:

$$\text{Rate } (\longrightarrow) = \text{Rate } (\longleftarrow)$$

$$k_1[\text{NH}_3] = k_2[\text{NH}_4^+][\text{OH}^-]$$

and the equilibrium constant for the weak base:

$$K_b = \frac{k_1}{k_2} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

(Note: Although the notation "eq" does not appear with each concentration, the equation is valid only when the concentrations are those of the same equilibrium system).



The expression for  $K_b$  is similar to the one for  $K_a$ . Just as dilution of a weak acid causes a greater per cent of ionization, so will dilution of a weak base. Again, with the addition of water, each concentration in the numerator is reduced by the same proportion as the one concentration in the denominator. To restore the value of  $K_b$  the  $[\text{NH}_3]$  must decrease with the consequent and equal increase in  $[\text{NH}_4^+]$  and  $[\text{OH}^-]$ .

The equilibrium constant expression, the Mass Law equation, is useful for quantitative calculations when the value of the constant  $K_b$  is known. This must be determined, using experimental data.

It happens that 0.1 M  $\text{NH}_3$  has a hydroxide concentration of 0.00135 M. That is, it has the same conductance, same bitter taste, is the same color with acid-base indicators and gives the same reading on the pH meter as 0.00153 M NaOH.

In 0.1 M  $\text{NH}_3$ :

$$[\text{OH}^-] = 0.00135 \text{ mole/liter}$$

$$[\text{NH}_4^+] = 0.00135 \text{ mole/liter (OH}^- \text{ and NH}_4^+ \text{ are formed together)}$$

The non-ionized ammonia concentration:

$$[\text{NH}_3] = 0.1 - 0.00135 \approx 0.1$$

Substituting the set of equilibrium concentrations in the expression:

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{0.00135 \times 0.00135}{0.1} = 1.82 \times 10^{-5}$$

By chance,  $K_b$  for ammonia and  $K_a$  for acetic acid have the same numerical value. One may now use the expression to find the hydroxide ion concentration and the pOH (analogous to pH) of various solutions containing ammonia.

**EXAMPLE 7.** Find the hydroxide ion concentration and the pOH of 0.30 M  $\text{NH}_3$ .

**SOLUTION:**

$$\text{Let } [\text{OH}^-] = X$$

$$\text{then } [\text{NH}_4^+] = X \quad (\text{both come from NH}_3, \text{ ion per ion})$$

the non-ionized ammonia concentration:

$$[\text{NH}_3] = 0.3 - X \approx 0.3$$

Substituting in the equation:

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{X \cdot X}{0.3} = 1.8 \times 10^{-5}$$

$$X^2 = 5.4 \times 10^{-6}$$

$$X = 2.3 \times 10^{-3} \text{ mole/liter} = [\text{OH}^-]$$

The pOH of the solution is found as follows:

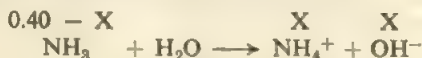
$$\begin{aligned}\text{pOH} &= 3 - \log 2.3 = 3.000 - 0.362 \\ &= 2.637\end{aligned}$$

EXAMPLE 8. Find the hydroxide concentration in a 500 ml solution containing 0.20 mole  $\text{NH}_3$  and 0.15 mole  $\text{NH}_4\text{Cl}$ .

SOLUTION: In moles per liter the concentrations are:

$$0.40 \text{ M } \text{NH}_3 \text{ and } 0.30 \text{ M } \text{NH}_4\text{Cl}$$

But  $\text{NH}_3$  is slightly ionized (X moles):



and  $\text{NH}_4\text{Cl}$  ionizes completely. A 0.30 M  $\text{NH}_4\text{Cl}$  solution contains 0.30 mole  $\text{NH}_4^+$  per liter and 0.30 mole  $\text{Cl}^-$  per liter and no un-ionized  $\text{NH}_4\text{Cl}$ .

The ionic concentrations from both substances are:

$$[\text{OH}^-] = X \text{ mole/liter}$$

$$[\text{NH}_4^+] = 0.30 + X \approx 0.30 \text{ mole/liter}$$

$$[\text{NH}_3] = 0.40 - X \approx 0.40 \text{ mole/liter}$$

$$[\text{Cl}^-] = 0.30, \text{ but is of no consequence in the problem.}$$

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{0.30 - X}{0.40} = 1.8 \times 10^{-5}$$

$$X = \frac{0.4}{0.3} \times 1.8 \times 10^{-5} = 2.4 \times 10^{-5} \text{ mole/liter}$$

$$[\text{OH}^-] = 2.4 \times 10^{-5} \text{ mole/liter}$$

$$\text{The } \text{pOH} = 5 - \log 2.4 = 5.00 - 0.382 = 4.618$$

The addition of  $\text{NH}_4^+$ , the conjugate acid of the base,  $\text{NH}_3$ , suppressed the hydroxide ion concentration. It is another example of common ion effect.

## H. FINDING SQUARE ROOTS

In several of the examples discussed and in several to follow, the square roots of numbers must be determined. An additional complication exists in that the number is a small fraction, often small enough that it is convenient to write it in exponential form. One thing to remember is that the product of the square roots of two numbers is the square root of their product. As an illustration:

$$4 \times 9 = 36$$

$$2 \times 3 = 6 \quad \text{Each number on the second line is the square root of the number above it.}$$

This is useful in finding the square roots of numbers in exponential form. The square root of

$$4 \times 10^{-6} \text{ is then}$$

$$2 \times 10^{-3}$$

Should the coefficient of ten be an uneven number, such as  $3.6 \times 10^{-7}$ , the decimal point must be moved since the coefficient must be divisible by 2.

$$3.6 \times 10^{-7} = 36 \times 10^{-8}$$

The square root is:

$$6 \times 10^{-4}$$

Unfortunately all numerical factors of exponential numbers are not perfect squares. The square root of that number may be found on a slide rule. Or, if one cannot read a slide rule, it may be determined using logarithms. The square root of a number is the number whose logarithm is one-half the logarithm of that number. For example:

- a. the log of 9 is 0.954; of 3 is 0.477
- b. the log of 4 is 0.602; of 2 is 0.301
- c. the log of 16 is 1.204; of 4 is 0.602

**EXAMPLE 9.** Find the square root of 7.1.

**SOLUTION:**

The log of 7.1 is 0.851 (Table 23.2).

$$\frac{0.851}{2} = 0.426$$

0.426 is nearest the logarithm of 2.7 (Table 23.2).

Answer: 2.7  
(Checking:  $2.7 \times 2.7 = 7.3$ )

2.7 is not the exact square root of 7.1, but it is near enough for our purposes.

**EXAMPLE 10.** Find the square root of  $2.4 \times 10^{-4}$ .

**SOLUTION:**

$$\text{The square root} = \sqrt{2.4} \times 10^{-2}$$

$$\text{logarithm of } 2.4 = 0.380 \text{ (Table 23.2)}$$

$$\frac{0.380}{2} = 0.190$$

The number whose logarithm is 0.190 is 1.6 (Table 23.2)

$$\sqrt{2.4} \times 10^{-2} = 1.6 \times 10^{-2}$$

Answer:  $1.6 \times 10^{-2}$

EXAMPLE 11. Find the square root of  $8.2 \times 10^{-11}$

SOLUTION:

$$8.2 \times 10^{-11} = 82 \times 10^{-12}$$

$$\text{Log } 82 = 1.914 \text{ (table)}$$

$$\frac{\text{Log } 82}{2} = \frac{1.914}{2} = 0.957$$

The number whose log is 0.957 is 9.1

$$\sqrt{82 \times 10^{-12}} = 9.1 \times 10^{-6}$$

Answer:  $9.1 \times 10^{-6}$

### I. Kw

Water is an interesting substance, for not only is it present in water solutions, but it is also both a weak acid and a weak base.

Water is often described as a non-conductor of electricity. In general, the statement is correct. But pure water has a very small but measurable conductance because of ionization:



This ionization is an equilibrium ionization. The rate of ionization is a function of the concentration of water:

$$\text{Rate} (\longrightarrow) = k[\text{H}_2\text{O}][\text{H}_2\text{O}]$$

but again because the water concentration suffers such a small change in dilute solutions of acids and bases, the rate is nearly constant:

$$\text{Rate} = k_1$$

$$\text{where } k_1 = k[\text{H}_2\text{O}]^2$$

The reverse rate is a function of the ionic concentrations.

$$\text{Rate} (\longleftarrow) = k_2[\text{H}_3\text{O}^+][\text{OH}^-]$$

At equilibrium:

$$\text{Rate} (\longrightarrow) = \text{Rate} (\longleftarrow)$$

$$k_1 = k_2[\text{H}_3\text{O}^+][\text{OH}^-]$$

$$\frac{k_1}{k_2} = [\text{H}_3\text{O}^+][\text{OH}^-] = K_w$$

There is no denominator in the equilibrium constant for water. This differs from all other weak acids, because water is the only acid that is its own solvent.

In the above rate equations  $k_2 \gg k_1$ ; that is to say, the concentrations of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  are very low in water. In very pure water, triple distilled in platinum ware, the hydronium ion concentration is equal to  $1.0 \times 10^{-7}$  mole/liter. The hydroxide ion concentration is also  $1.0 \times 10^{-7}$  mole/liter. Of the 55.5 moles of water present in 1 liter of pure water at or near room temperature, only  $1 \times 10^{-7}$  mole is ionized. This is justification for calling



water a covalent substance and a non-electrolyte. Actually some few ions are present.

If  $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1 \times 10^{-7}$  in pure water,

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1 \times 10^{-7} \times 1 \times 10^{-7} = 1 \times 10^{-14}$$

If this is true, neither  $[\text{H}_3\text{O}^+]$  nor  $[\text{OH}^-]$  can be zero in a water solution. If one is greater than  $1.0 \times 10^{-7}$ , the other must be less. In an acid solution, the  $[\text{H}_3\text{O}^+]$  is greater than  $1 \times 10^{-7}$ ; therefore the  $[\text{OH}^-]$  is less. Furthermore, when either  $[\text{H}_3\text{O}^+]$  or  $[\text{OH}^-]$  is known, the other can be determined, because their product is known.

EXAMPLE 12. Find the  $[\text{OH}^-]$  of 0.0024 M HCl.

SOLUTION: HCl is a strong electrolyte, therefore:

$$[\text{H}_3\text{O}^+] = 2.4 \times 10^{-3}$$

Substituting in  $K_w$ :

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 2.4 \times 10^{-3} \times [\text{OH}^-] = 1.0 \times 10^{-14}$$

$$[\text{OH}^-] = \frac{1.0 \times 10^{-14}}{2.4 \times 10^{-3}} = \frac{10 \times 10^{-15}}{2.4 \times 10^{-3}} = 4.2 \times 10^{-12}$$

### J. pH VERSUS pOH

Because the product of the hydronium ion concentration and the hydroxide ion concentration is always the same in a water solution, an interesting relationship exists between the pH and the pOH. Since one adds logarithms in multiplying:

if

$$[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

then

$$\log [\text{H}_3\text{O}^+] + \log [\text{OH}^-] = -14$$

and

$$-\log [\text{H}_3\text{O}^+] - \log [\text{OH}^-] = 14$$

or

$$\text{pH} + \text{pOH} = 14$$

Rearranging the equations:

$$\text{pH} = 14 - \text{pOH}$$

and

$$\text{pOH} = 14 - \text{pH}$$

EXAMPLE 13. Calculate the hydronium ion concentration, the hydroxide ion concentration, the pH and the pOH of 0.3 M HCN.  $K_{\text{HCN}} = 4.0 \times 10^{-10}$

SOLUTION:

a. To find  $[\text{H}_3\text{O}^+]$

let

$$X = [\text{H}_3\text{O}^+]$$

then

$$[\text{CN}^-] = X$$

and

$$[\text{HCN}] = 0.3 - X \approx 0.3$$

Substituting:

$$K_{\text{HCN}} = \frac{[\text{H}_3\text{O}^+][\text{CN}^-]}{[\text{HCN}]} = \frac{X^2}{0.3} = 4.0 \times 10^{-10}$$

$$X^2 = 1.2 \times 10^{-10}$$

$$X = \sqrt{1.2} \times 10^{-5}$$

$$\frac{\log 1.2}{2} = \frac{0.0792 \text{ (table)}}{2} = 0.0396$$

The number whose log is 0.0396 is 1.1:

$$X = 1.1 \times 10^{-5} \text{ mole/liter} = [\text{H}_3\text{O}^+]$$

b. to find  $[\text{OH}^-]$ :

$$[\text{H}_3\text{O}^+][\text{OH}^-] = 1.1 \times 10^{-5} \times [\text{OH}^-] = 1.0 \times 10^{-14}$$

$$[\text{OH}^-] = \frac{1.0 \times 10^{-14}}{1.1 \times 10^{-5}} = \frac{10 \times 10^{-15}}{1.1 \times 10^{-5}} = 9.0 \times 10^{-10} \text{ mole/liter}$$

c. to find the pH:

$$[\text{H}_3\text{O}^+] = 1.1 \times 10^{-5} \text{ mole/liter}$$

$$\text{pH} = 5 - \log 1.1 = 5.00 - 0.040 = 4.960$$

d. to find pOH

$$[\text{OH}^-] = 9.0 \times 10^{-10} \text{ mole/liter}$$

$$\text{pOH} = 10 - \log 9 = 10.00 - 0.954 = 9.046$$

or

$$\text{pH} = 4.960$$

$$\text{pOH} = 14.00 - 4.960 = 9.04$$

Pure water is neutral; it is the standard for neutrality. Any solution with the same hydronium ion concentration, or the same pH, or the same hydroxide ion concentration or the same pOH as water is neutral.

In pure water the hydronium ion concentration is the same as the hydroxide ion concentration.

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \text{ mole/liter}$$

and the

$$\text{pH} = 7 - \log 1 = 7.00$$

$$\text{pOH} = 7 - \log 1 = 7.00$$

The solution is neutral if the  $\text{pH} = 7$  and  $\text{pOH} = 7$

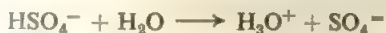
The solution is acidic if the  $\text{pH} < 7$  and  $\text{pOH} > 7$

The solution is basic if the  $\text{pH} > 7$  and  $\text{pOH} < 7$

## 2. HOMOGENEOUS EQUILIBRIA OF STRONG ELECTROLYTES

### A. HYDROGEN-SALT ACIDS

The hydrogen sulfate ion ( $\text{HSO}_4^-$ ), often called bisulfate ion, is an acid. It is obtained in solution by dissolving a hydrogen sulfate salt, such as sodium hydrogen sulfate ( $\text{NaHSO}_4$ ) in water. The salt dissociates completely in solution. The sodium ions make no contribution to the acidity of the solution. Hydrogen sulfate ion is an acid for this reaction occurs in water:



The hydrogen sulfate contributes a proton to water to form the hydronium ion. But hydrogen sulfate is only a moderately strong (and moderately weak) acid, for in a 1 molar solution of sodium hydrogen sulfate only about 1/10 of the bisulfate ions decomposes to form hydronium ions. Experiments with dilution and titration show the reaction to be reversible.



The equilibrium constant expression for the equation is:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]}$$

As always the concentration of water does not appear in the equation. For the hydrogen sulfate ion, the constant is  $1.26 \times 10^{-2}$ . One can use this constant to find the hydronium ion concentration and the pH of solutions containing the ion. However, the constant is so large that the quadratic equation must be solved.

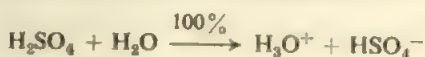
Many hydrogen-salt acids exist. Four appear in Table 23.5 with their constants.

**Table 23.5.**

<i>Acid</i>	<i>Reactions</i>	<i>Constant</i>
Bicarbonate ion	$\text{H}_2\text{O} + \text{HCO}_3^- \rightarrow \text{H}_3\text{O}^+ + \text{CO}_3^{2-}$	$4.8 \times 10^{-11}$
Bisulfate ion	$\text{H}_2\text{O} + \text{HSO}_4^- \rightarrow \text{H}_3\text{O}^+ + \text{SO}_4^{2-}$	$1.26 \times 10^{-2}$
Bisulfide ion	$\text{H}_2\text{O} + \text{HS}^- \rightarrow \text{H}_3\text{O}^+ + \text{S}^{2-}$	$1.3 \times 10^{-13}$
Dihydrogen phosphate ion	$\text{H}_2\text{O} + \text{H}_2\text{PO}_4^- \rightarrow \text{H}_3\text{O}^+ + \text{HPO}_4^{2-}$	$6.2 \times 10^{-8}$

The hydrogen sulfate ion is present in sulfuric acid solutions. Sulfuric acid is called a diprotic acid because it may donate two protons per molecule. The second proton is that of the hydrogen sulfate ion. The acidic properties of  $\text{HSO}_4^-$  are not so important in an  $\text{H}_2\text{SO}_4$  solution, because the contribution

to the hydronium ion concentration is negligible compared to that of the first (and 100%) ionization of  $\text{H}_2\text{SO}_4$ .



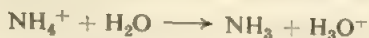
but



is an equilibrium reaction giving but a small concentration of hydronium ions. In general the second and third ionizations of diprotic and triprotic acids contribute little to the acidity of solutions of the acids, but do govern the acid concentration if present alone as a hydrogen salt.

### B. WEAK ACIDS AND BASES—HYDROLYSIS

The ammonium ion is a weak acid. A solution of an ammonium salt, such as ammonium chloride ( $\text{NH}_4\text{Cl}$ ), is slightly acidic. The solution is acidic and the ammonium ion is an acid since this reaction occurs:



The ammonium ions donate protons to water molecules. However, it is a weak acid, since the fraction of ammonium ions decomposed at any one time in an ammonium chloride solution is very small and changes with concentration.



The equilibrium expression for this reaction may be derived as before and is:

$$K_h = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]}$$

$K_h$  represents the constant for a hydrolysis reaction. This type of reaction is called hydrolysis (hydro-lysis, water decomposition). The distinction is not clear for the ionizations of all acids and all weak bases are water decompositions.

The equilibrium constant ( $K_h$ ) for this reaction might be evaluated as any other by the substitution of a set of equilibrium concentrations, but a mathematical trick makes this unnecessary:

$$K_h = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} = \frac{[\text{NH}_3][\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{NH}_4^+][\text{OH}^-]}$$

The fraction is not changed by multiplying both the numerator and denominator by the same quantity, the hydroxide ion concentration.

But

$$[\text{H}_3\text{O}^+][\text{OH}^-] = K_w$$

and

$$\frac{[\text{NH}_3]}{[\text{NH}_4^+][\text{OH}^-]} = \frac{1}{K_b \text{ for } \text{NH}_3}$$

$$K_h = \frac{K_w}{K_b}$$



The hydrolysis constant of the ammonium ion is equal to the equilibrium constant for water, divided by the ionization constant of its conjugate base, ammonia. A second look at the equation for the hydrolysis of ammonia suggests that  $K_w$  and  $K_b$  of ammonia are involved:



The equilibrium exists because  $\text{H}_2\text{O}$  on the left and  $\text{NH}_3$  on the right are competing for the proton. The equilibrium concentrations depend on the relative attraction of these two molecules for the proton in question.

The acetate ion is a weak base. Solutions of acetate salts, such as sodium acetate,  $\text{NaOAc}$ , are basic, since this reaction occurs:



and because the acetate ions accept protons from the water molecules. They are *weakly* basic, because only a small fraction of the acetate ions are converted to acetic acid molecules.

The equilibrium reaction may be represented by this equation:



The equilibrium expression is:

$$K_h = \frac{[\text{HOAc}][\text{OH}^-]}{[\text{OAc}^-]}$$

Again the reaction is called hydrolysis and, again, the constant for the acetate ion is related to the constant for water and the constant for the conjugate acid.

$$K_h = \frac{K_w}{K_a \text{ of HOAc}}$$

This is reasonable, because a glance at the equation reveals that  $\text{OAc}^-$  (on the left) competes with  $\text{OH}^-$  (on the right) for the proton to form  $\text{HOAc}$  or  $\text{H}_2\text{O}$ . Equilibrium concentrations are set by this competition. Just as the acetate ion,  $\text{OAc}^-$  (the conjugate base of acetic acid,  $\text{HOAc}$ ), is a base, so also are the hydrogen carbonate ion,  $\text{HCO}_3^-$  (the conjugate base of carbonic acid,  $\text{H}_2\text{CO}_3$ ); the cyanide ion,  $\text{CN}^-$  (the conjugate base of hydrocyanic acid,  $\text{HCN}$ ); the sulfate ion,  $\text{SO}_4^{2-}$  (the conjugate base of the acid hydrogen sulfate,  $\text{HSO}_4^-$ ).

The aluminum ion is also a weak acid. A solution of an aluminum salt, such as aluminum sulfate ( $\text{Al}_2(\text{SO}_4)_3$ ), is acidic because this equilibrium reaction occurs:



This and similar hydrolysis reactions will be discussed in a later chapter.

## C. BUFFER SOLUTIONS

In certain chemical systems, it is important to maintain a constant pH. The rates of reactions occurring in solutions are often dependent on the hydronium ion concentration. pH can affect the equilibrium concentration if the hydronium ion is a reactant. A change in pH may even alter the products of a reaction. Death results if the pH of the blood strays outside the pH limits of 6.8 to 7.8 (account is taken of this in intravenous feeding), but the blood of normal individuals contains a *buffer* that keeps the pH within the limits of 7.3 to 7.45. A buffer is a set of solution components that holds the pH nearly constant despite shocks to the system by relatively large additions of acids or bases.

To understand buffer action, consider addition of acid and base to three different solutions with the same pH:

**Solution A.** A dilute solution of a strong acid,  $1.8 \times 10^{-5}$  M HCl, has a pH of 4.75.  $[\text{H}_3\text{O}^+] = 1.8 \times 10^{-5}$

$$\text{pH} = 5.00 - \log 1.8 = 5.00 - 0.25 = 4.75$$

**Solution B.** A fairly concentrated solution of a weak acid, 0.8 M HCN ( $K_a = 4 \times 10^{-10}$ ), has a pH of 4.75:

If

$$X = [\text{H}_3\text{O}^+] = [\text{CN}^-]$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CN}^-]}{[\text{HCN}]} = \frac{X^2}{0.8} = 4 \times 10^{-10}$$

$$X = [\text{H}_3\text{O}^+] = 1.8 \times 10^{-5}$$

$$\text{pH} = 4.75$$

**Solution C.** A solution containing equal concentrations of a certain weak acid (stronger than HCN) and a salt of that weak acid, 1 M HOAc and 1 M NaOAc, has a pH of 4.75.

$$K_{\text{HOAc}} = 1.8 \times 10^{-5}$$

for if

$$X = [\text{H}_3\text{O}^+]$$

$$[\text{OAc}^-] = [1 + X] \text{ mole/liter} \approx 1$$

$$[\text{HOAc}] = (1 - X) \text{ mole/liter} \approx 1$$

$$K_a = \frac{X \cdot 1}{1} = 1.8 \times 10^{-5}$$

$$[\text{H}_3\text{O}^+] = X = 1.8 \times 10^{-5} \text{ mole/liter}$$

$$\text{and pH} = 4.75$$

Suppose to separate 1 liter volumes of each solution above are added:  
(a) 0.2 mole HCl and (b) 0.2 mole NaOH.

**Solution A.** To 1 liter of  $1.8 \times 10^{-5}$  M HCl with pH of 4.75 is added:

a. 0.2 mole HCl

$$0.2 \text{ mole/liter} + 0.000018 \text{ mole/liter} \approx 0.2 \text{ mole/liter}$$

$$[\text{H}_3\text{O}^+] = 2 \times 10^{-1}$$

$$\text{pH} = 1 - \log 2 = 1.000 - 0.301 = 0.699$$

b. 0.2 mole NaOH

$1.8 \times 10^{-5}$  mole of NaOH is used in neutralizing the HCl present, leaving  
 $0.2 \text{ mole/liter} - 0.000018 \text{ mole/liter} \approx 0.2 \text{ mole NaOH}$

$$[\text{OH}^-] = 2 \times 10^{-1} \text{ mole/liter}$$

$$\text{pOH} = 1.000 - \log 2 = 1.000 - 0.301 = 0.699$$

$$\text{pH} = 14.00 - 0.699 = 13.301.$$

**Solution B.** To 1 liter of 0.8 M HCN with a pH of 4.75 is added:

a. 0.2 mole HCl

The presence of more  $[\text{H}_3\text{O}^+]$  will just shift the equilibrium until a negligible amount of HCN is ionized.

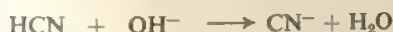
Even without this equilibrium shift the  $[\text{H}_3\text{O}^+]$  from HCN is negligible.

$$0.2 \text{ mole/liter} + 1.8 \times 10^{-5} \text{ mole/liter} \approx 0.2 \text{ mole/liter}$$

As before the pH is 0.699.

b. 0.2 mole NaOH. The 0.2 mole of NaOH neutralizes part of the acid present.

$$0.8 - 0.2 \quad 0.2 - 0.2 \quad 0.2$$



The concentrations are:

$$[\text{H}_3\text{O}^+] = X \text{ mole/liter}$$

$$[\text{CN}^-] = 0.2 + X \approx 0.2 \text{ mole/liter}$$

$$[\text{HCN}] = 0.6 - X \approx 0.6 \text{ mole/liter}$$

$$K_a = \frac{X \cdot 0.2}{0.6} = 4.0 \times 10^{-10}$$

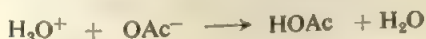
$$[\text{H}_3\text{O}^+] = X = \frac{0.6}{0.2} \times 4.0 \times 10^{-10} = 1.2 \times 10^{-9} \text{ mole/liter}$$

$$\text{pH} = 9 - \log 1.2 = 9.000 - 0.079 = 8.92$$

**Solution C.** To 1 liter of a solution containing 1 mole HOAc and 1 mole NaOAc per liter with a pH of 4.75 is added:

a. 0.2 mole HCl. The HCl added reacts with the acetate ion of the sodium acetate and is consumed, preparing:

$$0.2 - 0.2 \quad 1.0 - 0.2 \quad 1.0 + 0.2$$



0.2 mole of HOAc. If  $[\text{H}_3\text{O}^+]$  comes from the acetic acid:

$$[\text{H}_3\text{O}^+] = X \text{ mole/liter}$$

$$[\text{OAc}^-] = X + 0.8 \approx 0.8 \text{ mole/liter}$$

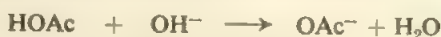
$$[\text{HOAc}] = 1.2 - X \approx 1.2 \text{ moles/liter}$$

$$K_a = \frac{X \cdot 0.8}{1.2} = 1.8 \times 10^{-5}$$

$$[\text{H}_3\text{O}^+] = X = \frac{1.2}{0.8} \times 1.8 \times 10^{-5} = 2.7 \times 10^{-5} \text{ mole/liter}$$

$$\text{pH} = 5 - \log 2.7 = 5.00 - 0.43 = 4.57$$

b. 0.2 mole NaOH. The  $\text{OH}^-$  from sodium hydroxide neutralizes some of the acetic acid present, preparing more acetate ions:



If  $[\text{H}_3\text{O}^+]$  comes from the acetic acid:

$$[\text{H}_3\text{O}^+] = X$$

$$[\text{OAc}^-] = 1.2 + X \approx 1.2 \text{ moles/liter}$$

$$[\text{HOAc}] = 0.8 - X \approx 0.8 \text{ mole/liter}$$

$$K_a = \frac{X \cdot 1.2}{0.8} = 1.8 \times 10^{-5}$$

$$[\text{H}_3\text{O}^+] = X = \frac{0.8}{1.2} \times 1.8 \times 10^{-5} = 1.2 \times 10^{-5} \text{ moles/liter}$$

$$\text{pH} = 5 - \log 1.2 = 5.00 - 0.079 = 4.92$$

The result of the addition of acid and base to separate portions of the three solutions is summarized in Table 23.6.

**Table 23.6. pH of Original Solutions and pH with Acid and Base Added**

Original Solution	pH		
	Original Solution	Original + 0.2 mole $\text{H}_3\text{O}^+$	Original + 0.2 mole $\text{OH}^-$
(A) 1.8 M HCl	4.75	0.699	13.301
(B) 0.8 M HCN	4.75	0.699	8.920
(C) 1 M HOAc, 1 M NaOAc	4.75	4.570	4.920

From the table one can see that the pH of a dilute solution of a strong acid (solution A) varied widely: 0.699—4.75—13.301. The solution of a very



weak acid (solution B) varied widely also: 0.699–4.75–8.92, although the pH did not rise as much with the addition of base as it did in solution A. Solution C, a solution of a moderately weak acid and its salt, is a buffer solution: the pH changed but little compared to the change in solution A and solution B: 4.57–4.75–4.92. The additions of acid and base were relatively large, but illustrate the buffer effect.

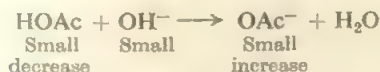
Acetic acid and the acetate ion are called a buffer-pair. A solution containing large and equal amounts of the two will have a hydronium ion concentration equal to the constant and will tend to keep the hydronium concentration near that, because the HOAc concentration and OAc<sup>-</sup> concentration control the H<sub>3</sub>O<sup>+</sup> concentration.

$$\frac{[\text{H}_3\text{O}^+][\text{OAc}^-]}{[\text{HOAc}]} = 1.8 \times 10^{-5}$$

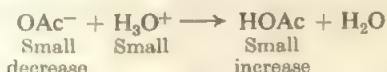
Observe the equilibrium constant equation. When both the acid and the anion concentrations are known the [H<sub>3</sub>O<sup>+</sup>] is set, when they are equal they divide out, and [H<sub>3</sub>O<sup>+</sup>] equals the constant.

$$\frac{[\text{H}_3\text{O}^+] \times \text{Equal}}{\text{Equal}} = 1.8 \times 10^{-5}$$

When [HOAc] and [OAc<sup>-</sup>] are *large* and equal, they tend to stay nearly equal, because the small amount of base added converts some HOAc to OAc<sup>-</sup>:



and small additions of acid convert some OAc<sup>-</sup> to HOAc:



*A solution containing any weak acid and its conjugate base in large equal concentrations is a buffer. Any weak acid and its conjugate base are a buffer-pair.* Each buffer tends to keep the H<sub>3</sub>O<sup>+</sup> concentration near the value of its particular equilibrium constant. Likewise any solution containing a weak base and its conjugate acid in relative large and equal concentrations is a buffer solution. *The weak base and its conjugate acid are a buffer-pair.* A solution 1 M in NH<sub>3</sub> and 1 M in NH<sub>4</sub>Cl tends to keep the [OH<sup>-</sup>] constant, the pOH constant and consequently the pH constant, because the ammonium concentration and ammonium ion concentration control the hydroxide ion concentration as shown in the equilibrium constant equation:

$$\frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5}$$

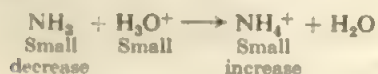
If they are equal:

$$\frac{\text{Equal} \times [\text{OH}^-]}{\text{Equal}} = 1.8 \times 10^{-5}$$

they divide out and the  $[\text{OH}^-]$  equals the constant. If they are large they tend to stay nearly equal, for a small addition of base converts a little ammonium to ammonia:



And a small addition of acid converts a small amount of ammonia to ammonium ion.



**Table 23.7. The pH of Certain Buffer Pairs**

<i>Pair</i>	<i>Constant</i>	<i>pH</i>
Acetic acid + acetate ion	$K_a = 1.8 \times 10^{-5}$	4.75
Carbonic acid + carbonate ion	$K_a = 4.2 \times 10^{-7}$	6.38
Hydrogen cyanide + cyanide ion	$K_a = 4.0 \times 10^{-10}$	9.40
Oxalic acid + oxalate ion	$K_a = 3.8 \times 10^{-2}$	1.42
Ammonia + ammonium ion	$K_b = 1.8 \times 10^{-5}$	9.25
Bisulfate + sulfate ion	$K_a = 1.26 \times 10^{-2}$	1.89

Table 23.7 lists a series of buffer-pairs, the constants of the acid or base and the pH of a solution containing equal concentrations of each of the pairs.

#### D. SUMMARY OF WEAK ACIDS AND BASES

At this point, as a conclusion of the discussion of weak acids and bases, certain relationships between the hydronium ion concentration, the hydroxide ion concentration, pH and pOH of certain solutions are summarized in graphic form in Table 23.8.

#### E. EQUILIBRIUM FORMATION AND DECOMPOSITION OF COMPLEX IONS

Certain metal ions in solution, especially those of the transition metals, tend to be surrounded by groups of molecules or other ions to form large complex ions. Many metal ions are hydrated in water solutions. The cupric ion is  $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ ; the aluminum ion,  $\text{Al}(\text{H}_2\text{O})_6^{3+}$ ; and the ferric ion,  $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ . For simplicity they are written as simply  $\text{Cu}^{2+}$ ,  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$ . Some commonly known complex ions are  $\text{Ag}(\text{NH}_3)_2^+$ , the diammine-silver ion;  $\text{Cu}(\text{NH}_3)_4^{2+}$ , the tetraamminecopper(II) ion;  $\text{Fe}(\text{CN})_6^{3-}$ , the hexacyanoferrate(III) ion;  $\text{Ag}(\text{S}_2\text{O}_3)_2^-$ , the dithiosulfatoargentate ion; and

Table 23.8. pH and pOH

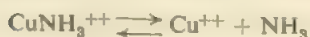
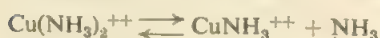
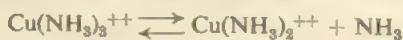
[H <sub>3</sub> O <sup>+</sup> ]	pH	Electrolytes		Common Ion	Hydrolysis	pOH	[OH <sup>-</sup> ]
		Strong	Weak				
10	-1	10 M HCl	1 M HSO <sub>4</sub> <sup>-</sup>	1 M HSO <sub>4</sub> <sup>-</sup> · 1 M SO <sub>4</sub> <sup>2-</sup>		15	10 <sup>-15</sup>
1	0	1 M HCl				14	10 <sup>-14</sup>
0.1	1	0.1 M HCl				13	10 <sup>-13</sup>
0.01	2	0.01 M HCl	1 M HOAc 0.1 M HOAc			12	10 <sup>-12</sup>
0.001	3	0.001 M HCl					
10 <sup>-4</sup>	4	1 × 10 <sup>-4</sup> M HCl				11	10 <sup>-11</sup>
10 <sup>-5</sup>	5	1 × 10 <sup>-5</sup> M HCl	1 M HCN	1 M HOAc · 1 M OAc <sup>-</sup>	1 M NH <sub>4</sub> <sup>+</sup> 1 M NaCl 1 M SO <sub>4</sub> <sup>2-</sup>	10	10 <sup>-10</sup>
10 <sup>-6</sup>	6		Water			9	10 <sup>-9</sup>
10 <sup>-7</sup>	7					8	10 <sup>-8</sup>
10 <sup>-8</sup>	8					7	10 <sup>-7</sup>
10 <sup>-9</sup>	9	1 · 10 <sup>-5</sup> M NaOH			1 M OAc <sup>-</sup>	6	10 <sup>-6</sup>
10 <sup>-10</sup>	10			1 M NH <sub>3</sub> + 1 M NH <sub>4</sub> <sup>+</sup> 1 M HCN + 1 M CN <sup>-</sup>		5	10 <sup>-5</sup>
10 <sup>-11</sup>	11	1 · 10 <sup>-4</sup> M NaOH 0.001 M NaOH				4	10 <sup>-4</sup>
			0.1 M NH <sub>3</sub> 1 M NH <sub>3</sub>		1 M CN <sup>-</sup>	3	0.001
10 <sup>-12</sup>	12	0.01 M NaOH				2	0.01
10 <sup>-13</sup>	13	0.1 M NaOH				1	0.1
10 <sup>-14</sup>	14	1 M NaOH				0	1
10 <sup>-15</sup>	15	10 M NaOH				-1	10
			K <sub>HOAc</sub> = 1.8 × 10 <sup>-5</sup> K <sub>NH<sub>3</sub></sub> = 1.8 · 10 <sup>-5</sup>	K <sub>HCN</sub> = 4 × 10 <sup>-10</sup> K <sub>H<sub>2</sub>SO<sub>4</sub></sub> = 1.26 · 10 <sup>-2</sup>			

$\text{FeSCN}^{++}$ , the thiocyanatoiron(III) ion. The prefixes di-, tri-, hexa- etc., indicate the number of groups (called ligands) about the metal ion center. The roman numeral indicates the oxidation state of the metal ion center.

Often metal-centered complex ions impart a characteristic color to a solution;  $\text{Cu}(\text{NH}_3)_4^{++}$  is an intense blue;  $\text{Cu}(\text{H}_2\text{O})_4^{++}$ , a powder blue;  $\text{FeSCN}^{++}$ , an intense red;  $\text{Fe}(\text{CN})_6^{--}$ , an amber. The nature of the bonding within a complex ion will be discussed later, along with a theory for the occurrence of color.

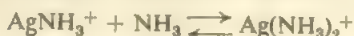
A complex ion is formed by a reversible and stepwise addition of ligands about the metal ion center until a stable maximum number is attained. The stable maximum number is characteristic of the metal center, although it can vary somewhat with the nature of the ligand. The formulas listed above indicate by sub-number the stable maximum ligand number, the so-called coordination number for the metal ion in the particular complex.

The reversible nature of the addition of ligands can be observed in a solution of cupric nitrate and ammonia. Gradual addition of ammonia in excess of that needed for complex formation causes a gradual deepening of the blue cast. Dilution of a tetraamminecopper(II) solution causes the color to fade more rapidly than the volume increases. In any solution with copper ions,  $\text{Cu}^{++}$  and ammonia, there are also these ions:  $\text{Cu}(\text{NH}_3)_4^{++}$ ,  $\text{Cu}(\text{NH}_3)_3^{++}$ ,  $\text{Cu}(\text{NH}_3)_2^{++}$  and  $\text{CuNH}_3^{++}$  related to one another by these equilibria:



A great excess of ammonia will shift all four equilibria (to the left as the equations are written) and cause most of the copper ion to appear as the tetraamminecopper(II) ion. With a smaller ammonia concentration all complex ions and cupric ions may appear in concentrations of the same order.

The diamminesilver(I) complex may be formed by adding ammonia to a solution of silver nitrate:



Both of the equilibria represented by the above equations have an equilibrium constant customarily shown for the reverse reaction.

$$\frac{[\text{Ag}^+][\text{NH}_3]}{[\text{AgNH}_3^+]} = 4.8 \times 10^{-4}$$

and

$$\frac{[\text{AgNH}_3^+][\text{NH}_3]}{[\text{Ag}(\text{NH}_3)_2^+]} = 6.3 \times 10^{-4}$$

One can use the constants to find equilibrium concentrations and to determine quantitatively the change in ionic concentrations with addition



of common ions and with dilution. But for this course, a qualitative understanding will suffice.

### 3. HETEROGENEOUS EQUILIBRIA

#### A. DISSOCIATION EQUILIBRIA

The mechanism of the dissolving of ionic substances was discussed in Chapter 17. Ions vibrating on the surface of a crystal in water are occasionally displaced sufficiently to be surrounded by water molecules with their strong dipoles and carried away into solution. If there were no return of ions to the crystal, all salts would be soluble in water until all the water molecules were used in hydration. Ions in the solution occasionally collide with the crystal face with sufficient force to push aside the surrounding water dipoles. If the ions rest at the right places on the lattice "checker-board" they are held and remain. Saturation occurs when the concentration of ions in solution becomes sufficiently great that the rate of return of ions to the crystal or crystals equals the rate of leaving. There is, then, no net change in the mass of the crystals. The solution is called a saturated solution. The concentration of the solute in the saturated solution is the solubility.

#### B. THE SOLUBILITY PRODUCT CONSTANT

Consider the rate equations for both the dissolving and precipitating (crystallizing) of a salt, silver chloride. Figure 23.5 illustrates the two rates.

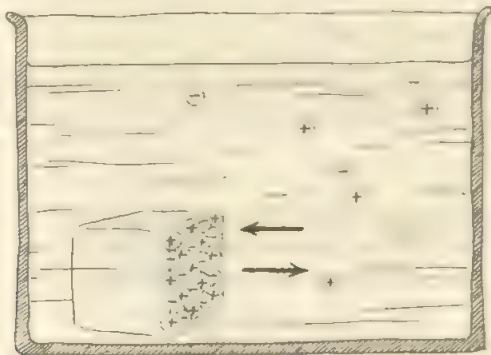


Figure 23.5. Rates in a saturated solution.

The rate at which a solid dissolves is dependent only on the temperature, which is constant (room temperature), and on the surface area of the crystal or crystals. That is:

$$\text{Rate } (\longrightarrow) = k_1 \times \text{area}$$

The rate at which ions return to the crystal (precipitation) is proportional to the surface area (the greater the surface area, the greater the number of collisions with the crystal), to the silver ion concentration and to the chloride ion concentration:

$$\text{Rate} (\leftarrow) = k_2 \times \text{area} \times [\text{Ag}^+][\text{Cl}^-]$$

Unless the solution is saturated, the rates may be unequal. At saturation the ionic concentrations will have adjusted themselves so that a dynamic equilibrium exists and:

$$\text{Rate} (\rightarrow) = \text{Rate} (\leftarrow)$$

$$k_1 \times \text{area} = k_2 \times \text{area} \times [\text{Ag}^+][\text{Cl}^-]$$

The crystal area appears in both rate expressions (because a greater area for leaving means a larger target to return to) and may be divided from the equation.

$$k_1 = k_2[\text{Ag}^+][\text{Cl}^-]$$

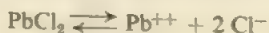
$$K_{sp} = \frac{k_1}{k_2} = [\text{Ag}^+][\text{Cl}^-]$$

$K_{sp}$  is the solubility product constant, the product of the solubilities (concentrations of the ions at saturation):

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-]$$

This expression indicates that the solubility of a salt depends only on the concentration of its ions. Further it indicates that one can decrease the concentration of one ion in solution by adding the other. Dilution reduces both ionic concentrations and therefore causes more salt to dissolve.

A variation appears in the solubility product expression when the positive and negative ions are not one to one in the crystal. To illustrate, the  $K_{sp}$  for lead chloride is thus derived:



The rate of dissolving of lead chloride is proportional to the area of the crystal or crystals at a set temperature and is not a function of any ion concentrations.

$$\text{Rate} (\rightarrow) = k_1 \times \text{area}$$

The rate of crystallization of the salt is proportional to the area, the concentration of lead ion and the concentration of chloride ion squared, because 2 chloride ions must precipitate with every lead ion:

$$\text{Rate} (\leftarrow) = k_2 \times \text{area} \times [\text{Pb}^{++}][\text{Cl}^-]^2$$

At equilibrium (saturation):

$$\text{Rate} (\rightarrow) = \text{Rate} (\leftarrow)$$

$$k_1 \times \text{area} = k_2 \times \text{area} \times [\text{Pb}^{++}][\text{Cl}^-]^2$$

and

$$K_{sp} = \frac{k_1}{k_2} = [\text{Pb}^{++}][\text{Cl}^-]^2$$

In the Mass Law Equation for equilibrium, each substance with a variable concentration appears in the power of its coefficient, the products in the numerator, the reactants in the denominator. The concentration of molecular

lead chloride ( $\text{PbCl}_2$ ) is very small. It is constant as long as any solid is present, and it does not appear in the expression.

### C. EVALUATION OF THE SOLUBILITY PRODUCT CONSTANT

The discussion above is a derivation of the solubility product constant. All one can say from that derivation is this, "If the rate of dissolving and the rate of crystallization are both proportional to the area of the crystals present at equilibrium, and if the rate of precipitation is proportional to the concentrations of the ions raised to the power of the coefficients in the balanced equation, the products of the solubilities of the ions of a salt raised to the power of the coefficients must equal a number which does not change unless the temperature is changed." The  $K_{sp}$  equation cannot be used quantitatively unless the value of the constant is known. This can be determined only by using a set of equilibrium concentration values.

The solubility of silver chloride is  $1.67 \times 10^{-5}$  mole/liter at room temperature. That is, solid silver chloride does not dissolve in a solution containing each of its ions at a concentration of  $1.67 \times 10^{-5}$  mole/liter. An equilibrium exists, a dynamic equilibrium.

Using these values, at equilibrium:

$$[\text{Ag}^+] = 1.67 \times 10^{-5} \text{ mole/liter}$$

$$[\text{Cl}^-] = 1.67 \times 10^{-5} \text{ mole/liter}$$

$$\begin{aligned} K_{sp} &= [\text{Ag}^+][\text{Cl}^-] = (1.67 \times 10^{-5})^2 \\ &= 2.8 \times 10^{-10} \end{aligned}$$

$1.59 \times 10^{-2}$  mole of lead chloride may be dissolved in 1 liter of pure water at room temperature. At that concentration the solution is saturated. Because the lead chloride forms ions according to this equation:



then  $[\text{Pb}^{++}] = 1.59 \times 10^{-2}$  mole/liter

and  $[\text{Cl}^-] = 2 \times 1.59 \times 10^{-2} \text{ mole/liter} = 3.18 \times 10^{-2} \text{ mole/liter}$

Substituting into the  $K_{sp}$  equation:

$$K_{sp} = [\text{Pb}^{++}][\text{Cl}^-]^2 = (1.59 \times 10^{-2})(3.18 \times 10^{-2})^2 = 1.6 \times 10^{-5}$$

### D. CALCULATIONS USING THE SOLUBILITY PRODUCT CONSTANT

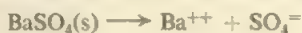
Once the  $K_{sp}$  is known, certain calculations can be made. One type is the reverse of the calculations above. If the  $K_{sp}$  is known, one can calculate the *solubility*.

**EXAMPLE 1.** Find the solubility of barium sulfate ( $\text{BaSO}_4$ ) in pure water. The  $K_{sp}$  of barium sulfate is  $1.0 \times 10^{-10}$ .

**SOLUTION:** At saturation:

$$[\text{Ba}^{++}][\text{SO}_4^{--}] = K_{sp} = 1.0 \times 10^{-10}$$

Let  $X$  equal the moles of barium sulfate dissolved per liter of solution. Because barium sulfate dissociates according to this equation:



$$\text{[Ba}^{++}\text{]} = \text{[SO}_4^{--}\text{]} = X$$

$$X^2 = 1.0 \times 10^{-10}$$

$$X = 1.0 \times 10^{-5} \text{ mole of BaSO}_4/\text{liter}$$

If the  $K_{sp}$  is known, one can find the solubility of a salt in a solution containing a *common ion*.

**EXAMPLE 2.** How many moles of  $\text{BaSO}_4$  will dissolve in 1 liter of 2 M  $\text{Na}_2\text{SO}_4$ ?

**SOLUTION:** Let  $X$  = moles of  $\text{BaSO}_4$  to dissolve per liter.  $K_{sp} = 1.0 \times 10^{-10}$

$$\text{Then } [\text{Ba}^{++}] = X$$

$$[\text{SO}_4^{--}] = 2 + X \approx 2$$

$$K_{sp} = [\text{Ba}^{++}][\text{SO}_4^{--}] = X \cdot 2 = 1.0 \times 10^{-10}$$

$$X = 5 \times 10^{-11}. \text{ The solubility of BaSO}_4 \text{ in the solution is } 5 \times 10^{-11} \text{ mole/liter.}$$

**Table 23.9. Solubility Product Constants at Room Temperature**

Substance	Equilibrium	Solubility Product Constant
Silver bromide	$\text{AgBr}_{(\text{s})} = \text{Ag}^+ + \text{Br}^-$	$3.3 \times 10^{-13}$
Calcium carbonate	$\text{CaCO}_{3(\text{s})} = \text{Ca}^{++} + \text{CO}_3^{--}$	$6.9 \times 10^{-9}$
Lead chloride	$\text{PbCl}_{2(\text{s})} = \text{Pb}^{++} + 2 \text{Cl}^-$	$1.6 \times 10^{-5}$
Mercurous chloride	$\text{Hg}_2\text{Cl}_{2(\text{s})} = \text{Hg}_2^{++} + 2 \text{Cl}^-$	$1.1 \times 10^{-18}$
Silver chloride	$\text{AgCl}_{(\text{s})} = \text{Ag}^+ + \text{Cl}^-$	$2.8 \times 10^{-10}$
Lead chromate	$\text{PbCrO}_{4(\text{s})} = \text{Pb}^{++} + \text{CrO}_4^{--}$	$2.0 \times 10^{-16}$
Silver chromate	$\text{Ag}_2\text{CrO}_{4(\text{s})} = 2 \text{Ag}^+ + \text{CrO}_4^{--}$	$1.9 \times 10^{-12}$
Calcium fluoride	$\text{CaF}_{2(\text{s})} = \text{Ca}^{++} + 2 \text{F}^-$	$3.6 \times 10^{-11}$
Aluminum hydroxide	$\text{Al}(\text{OH})_{3(\text{s})} = \text{Al}^{+++} + 3 \text{OH}^-$	$5 \times 10^{-33}$
Cupric hydroxide	$\text{Cu}(\text{OH})_{2(\text{s})} = \text{Cu}^{++} + 2 \text{OH}^-$	$1.6 \times 10^{-19}$
Ferric hydroxide	$\text{Fe}(\text{OH})_{3(\text{s})} = \text{Fe}^{+++} + 3 \text{OH}^-$	$6 \times 10^{-38}$
Silver iodide	$\text{AgI}_{(\text{s})} = \text{Ag}^+ + \text{I}^-$	$8.5 \times 10^{-17}$
Calcium oxalate	$\text{CaC}_2\text{O}_{4(\text{s})} = \text{Ca}^{++} + \text{C}_2\text{O}_4^{--}$	$1.3 \times 10^{-9}$
Barium sulfate	$\text{BaSO}_{4(\text{s})} = \text{Ba}^{++} + \text{SO}_4^{--}$	$1.0 \times 10^{-10}$
Lead sulfate	$\text{PbSO}_{4(\text{s})} = \text{Pb}^{++} + \text{SO}_4^{--}$	$1.3 \times 10^{-8}$
Cupric sulfide	$\text{CuS}_{(\text{s})} = \text{Cu}^{++} + \text{S}^{--}$	$4 \times 10^{-36}$
Ferrous sulfide	$\text{FeS}_{(\text{s})} = \text{Fe}^{++} + \text{S}^{--}$	$4 \times 10^{-17}$
Lead sulfide	$\text{PbS}_{(\text{s})} = \text{Pb}^{++} + \text{S}^{--}$	$4 \times 10^{-26}$
Mercurous sulfide	$\text{Hg}_2\text{S}_{(\text{s})} = \text{Hg}_2^{++} + \text{S}^{--}$	$1 \times 10^{-45}$
Silver sulfide	$\text{Ag}_2\text{S}_{(\text{s})} = 2 \text{Ag}^+ + \text{S}^{--}$	$1 \times 10^{-50}$



Compare the answers in Examples 1 and 2. Notice how the presence of the sulfate ion has suppressed the solubility of barium sulfate. Table 23.9 gives the solubility product constants for several common salts at room temperature.

### E. REPLACEMENT EQUILIBRIA

When a pure copper wire is placed in 3 M  $\text{AgNO}_3$ , silver precipitates on the copper and copper dissolves in the solution:



However all the silver is not taken from the solution; the reaction does not quite go to completion. When the silver ion concentration has been reduced to  $2.4 \times 10^{-8}$  molar, the copper sulfate concentration having risen to almost 1.5 molar, the reaction stops. Equilibrium has been attained.

The equilibrium constant expression for the equation (as long as some pure copper and pure silver are in contact with the solution) is:

$$K = \frac{[\text{Cu}^{++}]}{[\text{Ag}^+]^2} = \frac{1.5}{(2.4 \times 10^{-8})^2} = 2.6 \times 10^{15}$$

A cell may be constructed as shown in Figure 23.6. A copper electrode is placed in water containing a trace of  $\text{Cu}(\text{NO}_3)_2$ . The solution is separated by a porous plate from 3 M  $\text{AgNO}_3$  solution, in which a silver electrode is dipped. A relatively high voltage electric current flows when the electrodes are connected through the voltmeter. The voltage decreases until the cupric ion

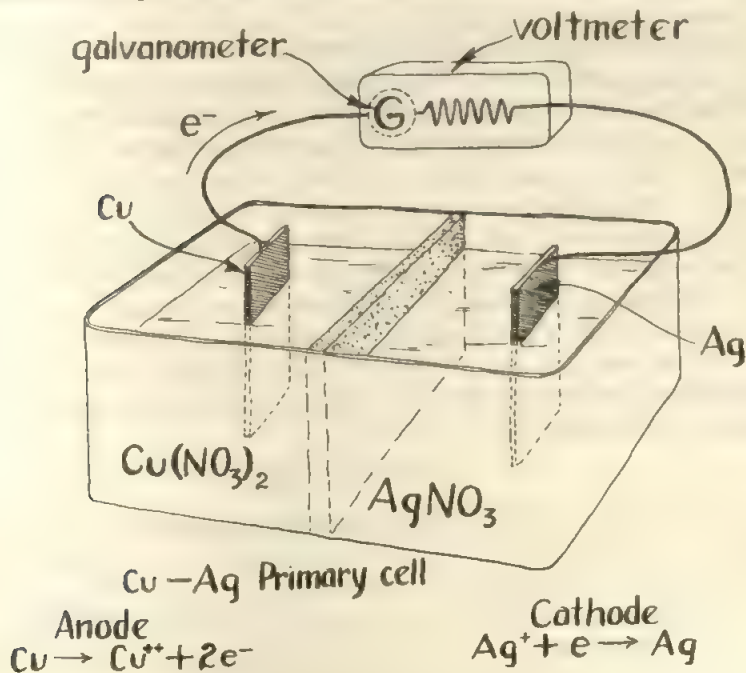


Figure 23.6 Cu-Ag primary cell.

concentration reaches 1 molar and the silver ion concentration has decreased to 1 molar. At these concentrations the voltage of the cell is 0.46 volt. The value found by subtracting the "voltage" values in the electromotive series (Table 19.1)  $-0.34 - (-0.80) = 0.46$  volt. As the reaction proceeds and the cell "runs down," the voltage decreases to zero at a silver concentration of  $2.4 \times 10^{-8}$  moles per liter. The system is at equilibrium; no force exists to change the concentrations.

The voltage 0.46 that exists for the silver-copper cell when both silver ion and cupric ion are 1 molar is a measure of the "unequilibrium." It is the force that must oppose the reaction to keep it from moving toward equilibrium conditions.

When chlorine gas is bubbled into a 2 molar sodium bromide solution, chlorine dissolves, replacing bromide. Bromine liquid collects on the bottom of the container.



The bromide ion is not completely replaced by the chlorine gas. If the atmospheric pressure and, therefore, the pressure of the chlorine is 1 atmosphere, the reaction stops when the bromide ion concentration is reduced to  $1.7 \times 10^{-5}$  mole per liter and the chloride ion concentration is nearly 2 molar.

The equilibrium constant expression may be written in this fashion:

$$K_{eq} = \frac{[\text{Cl}^-]^2}{P_{\text{Cl}_2}[\text{Br}^-]^2} = \frac{(2 \text{ moles/liter})^2}{1 \text{ atm } (1.7 \times 10^{-5} \text{ mole/liter})^2} = 1.37 \times 10^{10}$$

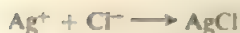
This reaction may be carried out in a cell. Chlorine gas at 1 atmosphere pressure is bubbled over a platinum electrode in 1 M NaCl solution separated by a porous plate from a 1 M NaBr solution with a drop of bromine liquid in the bottom and a platinum electrode in it. Current flows when the electrodes are connected; chlorine dissolves and the bromide ion is oxidized to bromine. The cell voltage is 0.30. 0.30 volt is a measure of the "unequilibrium." If the cell solutions were changed to  $1.7 \times 10^{-5}$  M NaBr and 2 M NaCl, no current would flow. In fact, if the electrodes are left connected, the reaction will proceed until these concentrations are reached.

In summary, displacement (oxidation-reduction) reactions are often reversible reactions. The cell voltage obtained from voltages in the electromotive force series are the measured voltages when all concentrations of participating ions are 1 molar. The voltage is a measure of the "unequilibrium" of the system.

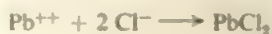
#### 4. COMPLEX EQUILIBRIA

It might be thought that the equilibria already considered are sufficiently complex. As a matter of fact, many of the equilibria may be much more complex than the equilibrium expressions indicate. In this section, processes will be discussed in which more than one reversible reaction is involved.

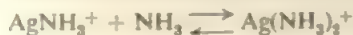
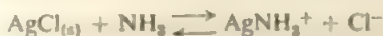
A. In many qualitative analysis schemes, the silver ion (along with the lead ion and the mercurous ion), is separated from other ions by the addition of hydrochloric acid. The silver ion precipitates as the chloride:



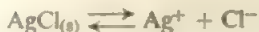
The lead and mercurous ions do likewise:



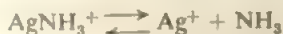
Lead chloride may be separated from the filtered precipitate of chlorides by the addition of hot water. (The solubility of lead chloride increases markedly with temperature.) Finally, silver chloride is separated from mercurous chloride by adding ammonia solution in which it is dissolved by formation of a complex ion:



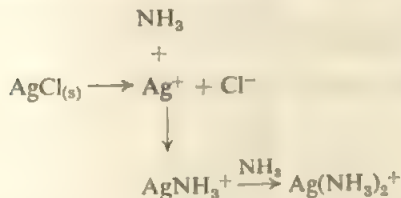
Before ammonia was added, an equilibrium existed between solid AgCl and the ions in solution:



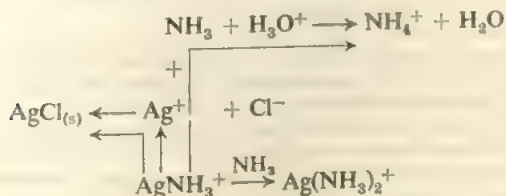
Because the  $K_{sp}$  of AgCl is small ( $2.8 \times 10^{-10}$ ), very low concentrations of  $\text{Ag}^+$  and  $\text{Cl}^-$  ions remain in solution at equilibrium. However, when ammonia is added, the concentration of silver ion is greater than can exist in equilibrium with silver ammonia complex ion:



Ammonia ties up the silver ion in an attempt to decrease the concentration to its equilibrium value. Silver chloride dissolves in an attempt to restore the silver ion concentration. If there is sufficient ammonia and if the chloride ion concentration does not become too great, all the AgCl dissolves.

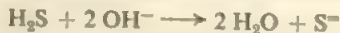


One can restore the AgCl precipitate by two ways: by increasing the chloride ion concentration or by decreasing the ammonia concentration. Both are accomplished by adding hydrochloric acid.



B. The separation of cupric ion and ferrous ion depends on the fact that, while both sulfides,  $\text{CuS}$  and  $\text{FeS}$ , will precipitate when  $\text{H}_2\text{S}$  gas is added to a basic solution containing the two ions  $\text{Fe}^{++}$  and  $\text{Cu}^{++}$ , only cupric sulfide ( $\text{CuS}$ ) precipitates from an acid solution.

Both sulfides are very insoluble;  $\text{CuS}$  is the least soluble. The  $K_{sp}$  for  $\text{FeS}$  is  $4 \times 10^{-17}$ ; for  $\text{CuS}$ ,  $4 \times 10^{-36}$ . In a 1 M  $\text{Cu}^{++}$  solution, the sulfide ion concentration cannot exceed  $4 \times 10^{-36}$  mole per liter. In 1 M  $\text{Fe}^{++}$  the sulfide ion concentration cannot exceed  $4 \times 10^{-17}$  mole per liter. A basic solution of hydrogen sulfide precipitates both ions, because it is no longer a solution of hydrogen sulfide, but a solution of sulfide:

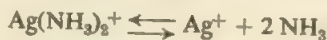


Hydrogen sulfide solution might contribute sulfide for precipitation. It is a weak electrolyte and is partially ionized in two steps.

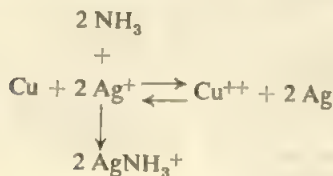


The first step occurs to a slight extent; the second to a much lesser degree, giving a sulfide ion concentration of  $1 \times 10^{-13}$  mole/liter in a neutral solution saturated with  $\text{H}_2\text{S}$  gas. As low as the sulfide concentration is, it is much greater than needed to precipitate either  $\text{CuS}$  or  $\text{FeS}$  from 1 molar solutions. In a 3 M  $\text{HCl}$  solution, an  $\text{H}_2\text{S}$  solution 3 molar in  $\text{H}_3\text{O}^+$ , the two ionization reactions of  $\text{H}_2\text{S}$  are forced to the left sufficiently that the sulfide ion concentration drops below  $4 \times 10^{-17}$  mole/liter (that needed to precipitate  $\text{FeS}$ ) and  $\text{CuS}$  is precipitated alone.

C. The precipitation of silver ion on copper wire from a 1 M  $\text{AgNO}_3$  solution may be stopped by adding ammonia solution. When the concentration of ammonia is above 2 molar the ammonia complex ties up the silver ions, reducing the concentration in solution below that needed for replacement with copper:



This is shown graphically in the "crossed" equation below:



### EXERCISES

1. Define: (a) homogeneous, (b) strong electrolyte, (c) equilibrium, (d) pH.
2. How might one show a solution to be a dilute solution of a strong electrolyte and not a more concentrated solution of a weak electrolyte?
3. What is the pH of: (a) water, (b) 0.001 M  $\text{HCl}$ , (c)  $2.4 \times 10^{-3}$  M  $\text{HNO}_3$ ?
4. A solution of a pure substance in water conducts an electric current. A solution of the same substance of twice the concentration is not twice as good a conductor as the first. Is the solution that of a strong electrolyte? Explain.



- Derive the equilibrium constant expression for the ionization of propionic acid (HOPr).
- Why are there no terms in the denominator of the expression for  $K_w$ ?
- Why is not a solution of sodium cyanide neutral?
- Solutions of which of these substances are weakly basic, but are good electrolytic conductors: (a)  $1 \times 10^{-3}$  M HCl, (b) 1 M  $\text{NH}_3$ , (c)  $\text{NH}_4\text{Cl}$ , (d)  $\text{NaOAc}$ .
- Derive the equilibrium constant expression for the ionization of the hydrogen sulfate ion ( $\text{HSO}_4^-$ ).
- Define hydrolysis. Write a hydrolysis reaction.
- Define buffer solution. Show why a solution containing 1 mole of formic acid and 1 mole of sodium formate per liter has a pH of 3.68.
- Write the decomposition equation for the cupric ammonia complex ( $\text{Cu}(\text{NH}_3)_4^{++}$ ).
- Derive the Ksp for the slightly soluble salt, silver chromate ( $\text{Ag}_2\text{CrO}_4$ ).
- Why does the voltage of a cell decrease in value as it discharges?
- Addition of which of the following will cause more silver chloride to dissolve in a saturated solution: (a) water, (b) 1 M HCl, (c) 1 M silver nitrate, (d) 6 M  $\text{NH}_3$ , (e) a zinc wire?
- Explain why  $\text{H}_2\text{S}$  gas bubbled into a solution containing 1 mole of  $\text{CuCl}_2$ , 1 mole of  $\text{FeCl}_2$  and  $\frac{3}{2}$  moles of HCl per liter will precipitate  $\text{CuS}$  and no  $\text{FeS}$ .

### PROBLEMS

- Calculate the ionization constant for germanic acid (represented as HGer). A 0.6 M solution has a hydronium concentration of  $1.34 \times 10^{-5}$ .
- Calculate the ionization constant for nitrous acid ( $\text{HNO}_2$ ), which in a 0.05 M solution has a hydronium ion concentration of  $4.7 \times 10^{-3}$  mole per liter.
- Calculate  $K_a$  for hyponitrous acid ( $\text{H}_2\text{N}_2\text{O}_2$ ). A 0.3 M solution has a hydronium ion concentration of  $1.7 \times 10^{-4}$  mole/liter.
- a. Write the ionic equation for the first ionization of silicic acid ( $\text{H}_4\text{SiO}_4$ ).  
b. Write the equilibrium constant expression.  
c. Calculate the ionization constant from the fact that a 0.2 M solution has a  $[\text{H}_3\text{O}^+]$  of  $1.4 \times 10^{-5}$ .
- Calculate the first ionization constant of sulfurous acid ( $\text{H}_2\text{SO}_3$ ) from the fact that a liter of solution containing 0.6 mole of  $\text{NaHSO}_3$  and 0.1 mole of  $\text{H}_2\text{SO}_3$  has a  $[\text{H}_3\text{O}^+]$  of  $2.0 \times 10^{-3}$ .
- Calculate the ionization constant of  $\text{NH}_3$ . A liter of solution containing 0.1 mole of  $\text{NH}_3$  and 0.1 mole of  $\text{NH}_4\text{Cl}$  has a hydroxide ion concentration of  $1.8 \times 10^{-5}$ .
- Calculate the  $[\text{H}_3\text{O}^+]$  of a 0.2 M  $\text{HBrO}$  solution.  $K_a = 2 \times 10^{-9}$ .
- Calculate the  $[\text{H}_3\text{O}^+]$  of a solution containing 2 moles of  $\text{HNO}_2$  and 0.4 mole of  $\text{NaNO}_2$  per liter.  $K_a = 4.5 \times 10^{-4}$ .
- Calculate the hydronium ion concentration in moles per liter in a solution containing 0.1 mole of propionic acid (HOPr) and 0.06 mole of sodium propionate ( $\text{NaOPr}$ ) per liter.  $K_a = 1.4 \times 10^{-5}$ .
- Calculate the  $[\text{OH}^-]$  of 5.5 M  $\text{NH}_3$ .
- Calculate the  $[\text{H}_3\text{O}^+]$  of 4 M  $\text{HCN}$ .  $K_a = 4 \times 10^{-10}$ .
- Calculate the hydronium ion concentration of 3.2 M  $\text{HOAc}$ .
- For a 2 M  $\text{NH}_3$  solution, calculate: (a)  $[\text{OH}^-]$ , (b)  $\text{pOH}$ , (c)  $[\text{H}_3\text{O}^+]$ , (d) pH.
- For a solution containing 2.4 moles of  $\text{NH}_4\text{Cl}$  and 1.2 moles  $\text{NH}_3$  per liter calculate: (a)  $[\text{OH}^-]$ , (b)  $\text{pOH}$ , (c)  $[\text{H}_3\text{O}^+]$ , (d) pH.
- Calculate the pH of all solutions described in Problems 7 to 11.
- A saturated solution of silver bromide has a concentration of  $5.75 \times 10^{-7}$  mole per liter. Calculate the solubility product constant. Ans:  $3.3 \times 10^{-13}$
- A saturated solution of silver iodide is  $9.2 \times 10^{-9}$  M. Calculate the Ksp. Ans:  $8.5 \times 10^{-17}$
- Calculate the Ksp for calcium fluoride. Calcium fluoride has a solubility of  $2.04 \times 10^{-4}$  mole per liter. Ans:  $3.4 \times 10^{-11}$
- Calculate the Ksp for  $\text{Ag}_2\text{S}$ , knowing that it has a solubility of  $1.58 \times 10^{-24}$  mole per liter in a  $1.0 \times 10^{-3}$  molar solution of sodium sulfide. Ans:  $1.0 \times 10^{-50}$
- Calculate the Ksp for  $\text{Ag}_2\text{S}$ . The solubility of  $\text{Ag}_2\text{S}$  is  $1.35 \times 10^{-17}$  mole per liter. Ans:  $1.0 \times 10^{-50}$
- Calculate the solubility of  $\text{BaSO}_4$  in a 2 M solution of  $\text{BaCl}_2$ .  $K_{sp} = 1 \times 10^{-10}$ . Ans:  $5 \times 10^{-11}$

22. Calculate the solubility of  $\text{BaSO}_4$  in moles per liter.  
Ans:  $1.0 \times 10^{-5}$
23. Calculate the concentration of sulfide ion necessary to just start precipitation of  $\text{FeS}$  from a 0.1 M solution of  $\text{FeCl}_2$ .  $K_{sp}$  of  $\text{FeS} = 4 \times 10^{-17}$ .  
Ans:  $4 \times 10^{-16}$
24. The  $[\text{H}_3\text{O}^+]$  of 0.05 M  $\text{HCN}$  is  $4.5 \times 10^{-6}$ . Calculate the equilibrium constant,  $K_a$ , for  $\text{HCN}$ .  
Ans:  $4.0 \times 10^{-10}$
25. Calculate  $K_a$  for  $\text{HNO}_2$ . A 0.05 M solution has a  $[\text{H}_3\text{O}^+]$  of  $4.7 \times 10^{-3}$  (0.0047) mole per liter.  
Ans:  $4.9 \times 10^{-4}$
26. Calculate the ionization constant,  $K_b$ , of  $\text{NH}_3$  ( $\text{NH}_4\text{OH}$ ) if a 0.1 M solution has an  $[\text{OH}^-]$  of  $1.34 \times 10^{-3}$  mole/liter.  
Ans:  $1.8 \times 10^{-5}$
27. Calculate the  $[\text{H}_3\text{O}^+]$  of 0.01 M  $\text{HCN}$ .  $K_a$  for  $\text{HCN}$  is  $4.0 \times 10^{-10}$ .  
Ans:  $2.0 \times 10^{-6}$
28. Calculate the  $[\text{H}_3\text{O}^+]$  of a solution 0.1 M in  $\text{HCN}$  and 0.1 M in  $\text{NaCN}$ .  
Ans:  $4.0 \times 10^{-10}$
29. Calculate the  $[\text{OH}^-]$  of a solution containing 0.2 mole of  $\text{NH}_3$  and 0.4 mole of  $\text{NH}_4\text{Cl}$  per liter.  
Ans:  $9 \times 10^{-9}$

# CHAPTER 24

## COLLOIDS

### 1. INTRODUCTION

A colloid is a "near solution" composed of at least two substances which are insoluble in one another. Tiny particles of one substance are dispersed throughout the other as are particles of a solute throughout the solvent in a solution. Both, the solution and the colloid, appear with the unaided eye as homogeneous pure substances. In a true solution, the solute particles are individual atoms, molecules or ions. The solute, being soluble in the solvent, separates into these ultimate particles. In contrast, the particles in a colloid are much larger and generally consist of groups or clusters of many molecules or ions. Few exceptions to this exist, except for gigantic polymer molecules such as may be found among proteins or polysaccharides which may constitute a single particle. A colloid thus contains two phases: the dispersed phase and a continuous phase in which the particles are distributed. For reasons to be discussed later, the tiny particles of a dispersed phase do not clump together (coalesce) and settle out.

As stated previously, particles of the dispersed phase of a colloid are normally invisible. They range in diameter from  $10^{-4}$  to  $10^{-7}$  cm. The presence of particles is evident when a path of light through the mixture is observed at right angles. A cloudy cylinder appears, known as the Tyndall effect (Fig. 24.1). The individual particles that together present a cloudy appearance can be detected by an ultramicroscope. An ultramicroscope is merely a microscope trained on an individual particle in the Tyndall column. The reflected light from the particle, when viewed in the field of the ultramicroscope, moves at random showing the particle to be in Brownian motion.

The unique properties of a colloid may be attributed both to the minute

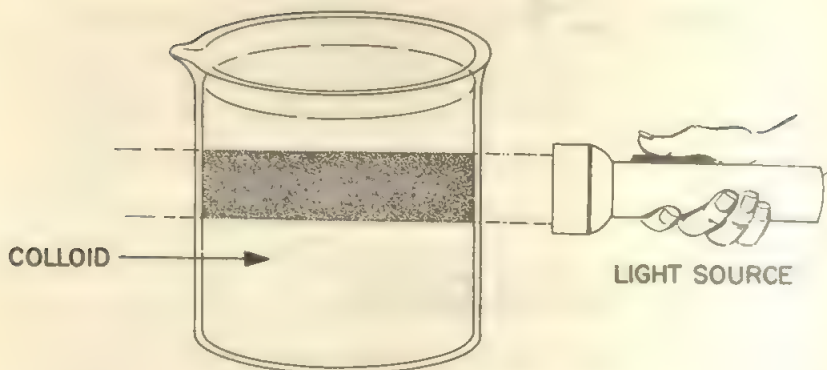


Figure 24.1. The Tyndall effect.

size of the dispersed particles, which, because of their tiny size, do exhibit unusual properties, and to the wide dispersion of the particles in the supporting phase. The unusual properties of small particles will be discussed first. The types of colloids which form as various particles are dispersed in different media will then be considered.

## 2. PROPERTIES OF SMALL PARTICLES

One might assume that small particles of a pure substance should have properties identical with those of larger clusters. This is not true of individual ions or molecules, compared to the larger aggregates. Silver nitrate in a solution, when mixed with a solution of sodium chloride, reacts instantaneously to precipitate silver chloride. However, dry crystals of the two solids can remain indefinitely in intimate contact without reacting. Though not as marked as this, differences do exist between colloidal-sized particles and still larger aggregates. Properties influenced by particle size include color, solubility, vapor pressure and ability to absorb other substances.

### A. COLOR

When powdered, a substance may change in color. Finely divided metals appear jet black. Platinum powder precipitated from a solution for use as a catalyst is called platinum black. Mercuric sulfide precipitated from a mercuric nitrate solution with hydrogen sulfide,  $\text{H}_2\text{S}$ , may appear black, green or blue depending upon particle size. A colorless salt crystal, when powdered, appears white. Undoubtedly, the scattering of light by the multitude of randomly oriented particle faces has much to do with the apparent change in color.

### B. SOLUBILITY

Tiny particles exhibit a slightly greater solubility than larger particles. One takes advantage of this property when a precipitate is allowed to digest



before filtering. Often tiny colloid particles, small enough to pass through the pores of a filter, will, upon standing (or better, upon standing at a higher temperature), disappear as larger particles form and grow larger.

Very tiny particles of the order of a few molecules or ions, must have a predominance of convex surfaces (Fig. 24.2). Ions or molecules at this surface have fewer attracting neighbors than those in a plane or nearly plane surface, are held less tightly and leave more readily and, thus, at a greater rate. These particles, therefore, can exist in equilibrium with a more concentrated solution than larger particles.

### C. VAPOR PRESSURE

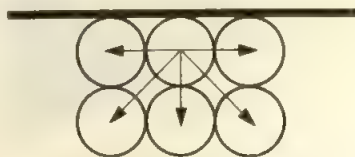
Tiny particles or tiny droplets have a slightly greater vapor pressure than larger bodies of the same substance. The convex surfaces where each molecule has fewer neighbors account for the increase in vapor pressure. One problem in laying out poison gas in wartime (most poison gases are liquids and are laid down as mists) is to perfect a spray that will deliver tiny droplets all of the same size. Such a mist, under the right conditions, could remain for weeks or longer in a little valley or pocket of undisturbed air. The liquid vaporizes and condenses at the same rate from each drop, keeping them at constant size.

### D. ABSORBENCY

Fine particles often have a great degree of absorbency. A large volume of carbon monoxide can be absorbed on a few cubic centimeters of activated charcoal. Activated charcoal is a very porous material, an aggregate of tiny particles. The property of great absorbency depends upon the greater surface area. One cubic centimeter of solid absorbent material has  $6\text{ cm}^2$  area of absorbent surface. The same cube divided into cubes  $0.001\text{ mm}$  on an edge has a total surface area of  $60,000\text{ cm}^2$  and should therefore absorb approximately 10,000 times the material absorbed by the single cube. Cornstarch powder dusted on a grease spot on fabric will often absorb the spot and remove it when brushed out because of the large absorbent surface of the tiny starch particles.



Figure 24.2. Surfaces of tiny and larger particles.



### 3. TYPES AND BEHAVIOR OF COLLOIDS

#### A. AEROSOL

One common type of colloid, more common than first supposed is the aerosol. An aerosol is composed of tiny particles, solid or liquid, dispersed in a gas phase. The most common continuous phase is air. Ordinary air is a dilute aerosol. The existence of tiny particles in the air can be seen in shafts of sunlight in a darkened building.

Mists, fogs and clouds are aerosols of tiny water droplets in air. A cloud may exist for hours or days and yet not condense to rain or snow.

One reason for the great stability of clouds is the fact that each particle (each droplet) may bear a charge. As a cloud brushes over the surface of the earth, polar points in clay particles may attract electrons from the droplets. The positive droplets formed then repel one another and cannot come together. If the droplets are of constant size with equal vapor pressures, all will remain, losing and gaining equally and the aerosol is stable and remains (Fig. 24.4). However, when the particle charge is neutralized by lightning (electrons traveling up from the earth's surface) the neutralized droplets can collect and fall.

Cloud seeding is based upon the principle that the large negative iodide ion of silver iodide will attract and collect the positive droplets around it. Becoming large, the droplet formed about the ion falls, collecting others on the way down. (The falling droplets give a conducting path for the neutralization from the earth's surface and the rain falls.)

Fine dust from parched, over-grazed or over-tilled land may be swept up from the earth to form a huge aerosol (dust cloud). In the sweeping-up process, electrons are lost to the earth's surface. The charged particles repel

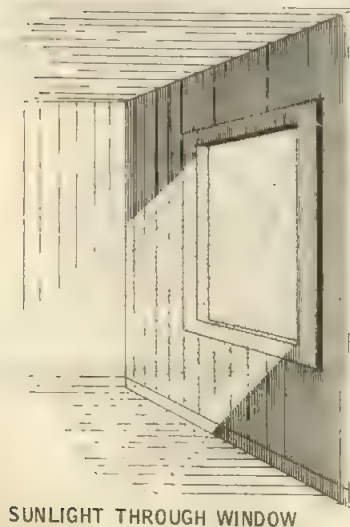


Figure 24.3. Particles in light rays.

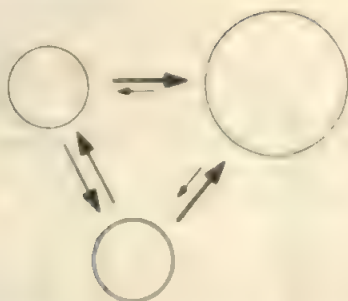


Figure 24.4 Cloud droplets.

one another. Such clouds have been known to remain in the air for days and to travel for hundreds of miles with the prevailing winds. Ships at sea have been deluged with muddy rains when a dust cloud, neutralized in an electrical storm, comes down with the rain.

Because air contains oxygen, aerosols of combustible material may be explosive. Flour mills have been blown to bits by ignition of flour dust in air. Coal dust remaining after blasting in a coal mine may be ignited by a spark, causing an explosion in which miners and equipment are hurled from a mine as if shot from a cannon's mouth. Explosion danger exists in these cases because the combustible material and oxygen are both present. Furthermore the tiny isolated colloid particles can be heated to the kindling temperature by even the smallest spark. Once ignited, the rapidly burning particles heat more and more neighboring particles to the ignition temperature and the explosion spreads.

### B. SOL

The term sol is used in the general sense to designate a dispersion of a solid in a solid, gas or liquid. Of these types, the class in which tiny solid particles are dispersed in liquid is by far the most important. The discussion which follows, unless otherwise stated, refers to this type of sol.

A sol exhibits the Tyndall effect. A cloudy path can be seen when a beam of light is passed through it in a darkened room. Each particle of the cloudy path can be seen to execute Brownian motion when viewed with an ultramicroscope. A sol can be prepared by shaking finely powdered clay in water. Minute particles remain suspended. At times, when attempting to precipitate solids in the laboratory, the solid forms as a sol having particles so small as to pass through the pores of a filter paper. Digesting the precipitate (mentioned above) often helps. Often adding a salt such as ammonium nitrate helps to collect sol particles into filterable-sized aggregates by neutralizing the charge on the particles. Sol particles may be charged by either having lost ions to or having absorbed ions from the solution. The charged particles sometimes collect about the ions of opposite charge.

One important class of sols is protein solutions. Much research work is being done on proteins. Tissue is broken down and the proteins extracted with water. The protein molecules are often of sol particle size. To study

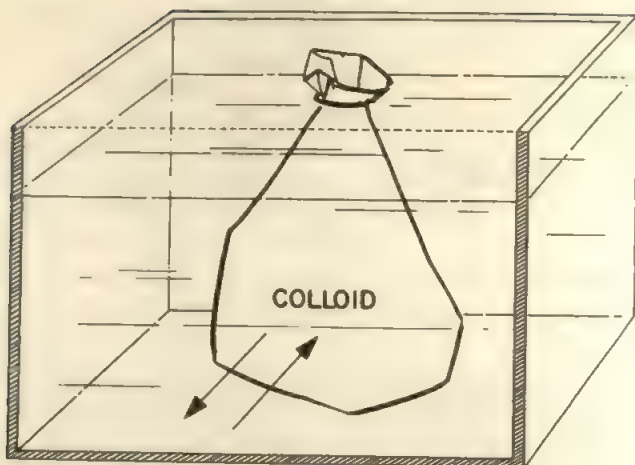


Figure 24.5. Dialysis.

the proteins one must separate the protein from ions in the solution and then separate the sol mixtures into near-homogeneous fractions of proteins without taking them out of the water medium or causing them to become denaturated (permanently changed). An ultracentrifuge will precipitate colloid particles, and because they precipitate in order of decreasing mass it permits their separation and classification according to size, leaving the ions behind in solution. One can also remove ions by dialysis. For dialysis the colloid solution is placed in a bag having a membrane permeable to ions but not to sol particles. The bag is placed in distilled water. Ions move through the membrane until the concentration is nearly equal in and out (Fig. 24.5). This reduces the ion concentration inside the bag. A series of successive dialyses, each in distilled water, reduces the concentration of ions greatly.

### C. GELS

A gel contains solid particles dispersed in a liquid. A gel also exhibits the Tyndall effect. Gel particles, however, are not near-spherical particles as are most sols, but are tiny fibers—fibers that are interconnected. In a sense the solid is a continuous phase, like a “honeycomb” in a beehive. The network is three-dimensional with the fibers so close together that the liquid becomes trapped between them. The trapping of the liquid increases the viscosity greatly, and the liquid is not free to flow.

Jelly and gelatin deserts are gels and possess the semi-rigid form characteristic of gels. The continuous liquid phase is water and the fibers are extracted from the joints of animal hoofs, purified and dried. Gels often appear in chemical processes where molecules combine in branched chains and networks. The solid itself is, of course, only a very small fraction, by weight, of the complete gel.



## D. EMULSION

An emulsion is composed of two immiscible liquids. Droplets of one liquid are dispersed throughout the other. The proportion of the dispersed liquid and continuous liquid can vary greatly. Emulsions with a high proportion of dispersed liquids often appear creamy or milky. Most emulsions contain water as one liquid. The second liquid must be immiscible and is often called the oily liquid or the oil.

Milk is both a sol and an emulsion. Protein and other solids form the sol part, and droplets of fat which collect and rise eventually as cream constitute the oily phase of an emulsion.

An emulsion may contain either oil droplets in water or water droplets in oil. That is, either phase may be the continuous phase (Fig. 24.6). One can not always determine which is the continuous from the appearance. However, if dissolved salts are present, one can determine the type experimentally. If an emulsion containing ions conducts an electric current, the continuous phase is water. If it does not, the ions are in isolated droplets and cannot pass freely through the solution (Fig. 24.6).

Salad dressings and cream hair oil are emulsions. Cream hair oil is easily spread on the hair. It is an oil in water emulsion. Water can enter the continuous water layer and thin it out indefinitely. Oil alone cannot be wet and will not mix with the water.

Preparation of a permanent emulsion may be rather difficult. One can shake two liquids together vigorously until small droplets are mixed together. But as soon as agitation ceases, the liquids often separate into layers of the two liquids. The colloid can often be stabilized by adding an emulsifying agent. An emulsifying agent has a dual aspect, a water and an oil aspect. Soap and synthetic detergents are emulsifying agents. As described in Chapter 35 the soap molecule has a long oily end and a short ionic end. The oily end dissolves in oil, the ionic end in water. When the two, oil and water, are shaken together with soap, the soap molecules line up around the droplets in the surface between the two phases. A bond of attraction forms between the liquids and they remain mixed.

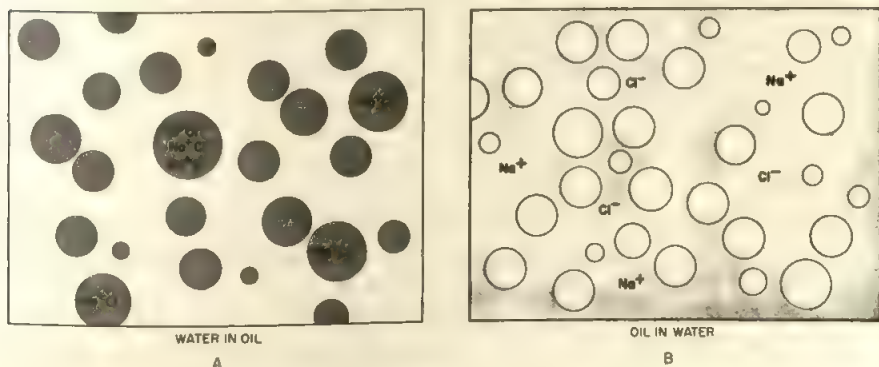


Figure 24.6. The two types of emulsions.

Salad dressing and cream hair oil contain emulsifying agents. Modern automobile engine oil contains a detergent, so that any water in the crankcase is taken up in the form of colloidal particles and removed when the oil is changed.

### EXERCISES

1. Define a colloid.
2. Define: (a) a gel, (b) a sol, (c) an aerosol, (d) an emulsion.
3. What stabilizes a dust cloud (an aerosol) so that the dust may remain aloft for days?
4. Why is a dust cloud often broken up in an electrical storm?
5. Is a snowflake a collection of colloid particles, or does it occur as an enlargement of one colloidal particle? Explain.
6. Fine amber-colored glass is a sol of gold dispersed in a supercooled liquid. Why the color?
7. Why should aluminum particles blown in air explode when ignited?
8. Why will ducks sink in a pool with detergent added?
9. Name four emulsions.
10. Why is a sol of equal-sized particles in a saturated solution more stable than one with a gradation in sizes?
11. Why is a gel more viscous than a sol?
12. Why should a small droplet of water have a higher vapor pressure than a large drop?
13. A large drop of water, a large drop of salt solution and several small drops of water on a glass plate are placed in an airtight container saturated with water vapor. What happens eventually?
14. Why should milk containers be covered when placed in a refrigerator?
15. Milk is homogenized by passing it, under pressure, through a microsieve. What does this process accomplish?

# METALLURGY OF THE COMMON METALS

## 1. THE COMMON METALS

Metals are discussed in previous chapters. In Chapter 7 they are defined as those elements that tend to lose electrons in chemical reactions. They are shown to occupy the lower left two-thirds of the Periodic Table (Table 25.1).

Table 25.1. The Common Metals

H																	Non-Metals						He
Li	Be																	B	C	N	O	F	Ne
Na	Mg	Metals																Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr						
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe						
Cs	Ba	La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn						
Fr	Ra	Ac-Lu																					

In Chapter 14 the active metals, those which are most metallic according to the chemical definition and have the least attraction for electrons, are discussed. In that chapter the physical properties of metals are listed. These general properties, hardness, ductility, malleability, tensile strength, conductivity, etc., apply more generally to the metals to be discussed here than to the active metals.

The symbols of the common metals are underlined in the representation of the Periodic Table (Table 25.1). Among them are iron (Fe), copper (Cu), silver (Ag), chromium (Cr), vanadium (V), nickel (Ni), tungsten (W), aluminum (Al), tin (Sn) and lead (Pb). These elements are recognized as metals by even the non-chemist.

This chapter discusses the industrial methods of obtaining and treating the common metals. Metals generally occur in nature as minerals, naturally occurring metal-containing compounds. These compounds are mixed with rock and often buried beneath the earth's surface. An ore is a mineral deposit of sufficient mineral content and of such a physical state as to be economically extracted.

The main topics to be discussed here are: (1) the mining of the ore, (2) the separation of inert rock material from the ore, (3) the reduction of the compound to yield the free metal, (4) the refining, or purification, of the metal and (5) the addition of other metals or substances to prepare alloys, with emphasis on the chemistry involved in the reduction and refining processes.

These five metallurgical steps are accomplished in a variety of ways, and the order of the steps may be changed in the processing of different metals. In the processing of some metal ores, the steps occur simultaneously. In other processes, each step is composed of several smaller steps. Variations in the process are as numerous as the number of metals, hence it is impossible to describe the metallurgy of all the common metals. As a compromise, the metallurgy of six metals will be discussed quite thoroughly. These metals—magnesium, aluminum, copper, iron and silver and gold—are chosen because they present the three most important different metallurgical schemes and they are the most important individual metals.

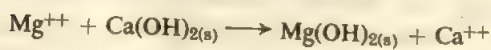
## 2. METALLURGY

### A. MAGNESIUM

The method of extracting magnesium from sea water is interesting. The per cent magnesium in sea water is low—0.13 % or 2.6 pounds per ton. Despite the low concentration, the amount available is tremendous. One cubic mile of ocean water contains nearly 6,000,000 tons of magnesium, and there are 300,000,000 cubic miles of water in the oceans.

Magnesium occurs as an ion ( $\text{Mg}^{++}$ ) in sea water. With it are the ions sodium ( $\text{Na}^+$ ), potassium ( $\text{K}^+$ ), chloride, ( $\text{Cl}^-$ ) and sulfate ( $\text{SO}_4^{--}$ ) and others. Magnesium must be separated from the other ions present, reduced and purified. This is done in three major steps.

- (1) A slurry of slaked lime ( $\text{Ca}(\text{OH})_2$ ) is added to large vats of sea water. Magnesium hydroxide is less soluble than calcium hydroxide and therefore precipitates as the calcium hydroxide dissolves:

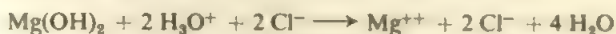


Because sodium hydroxide and potassium hydroxide are both very



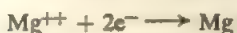
soluble, the two positive ions remain in solution along with the sulfate, the chloride and the added calcium ions.

- (2) After filtration the magnesium hydroxide precipitate is converted to a solution of magnesium chloride by dissolving in hydrochloric acid:

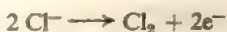


Upon evaporation and drying, a salt of the approximate composition  $\text{MgCl}_2 \cdot 1.25 \text{H}_2\text{O}$  is obtained.

- (3) Finally, that salt is electrolyzed from a melt containing 25%  $\text{MgCl}_2$ , 15%  $\text{CaCl}_2$  and 60%  $\text{NaCl}$  at  $700^\circ\text{C}$  in a cell kept hot by external heating and electrical resistance. The more active metal ions, sodium and calcium, remain in the melt, while the magnesium ion is reduced at the walls, which serve as the cathode, and rises to collect as a pool of molten metal at the surface:

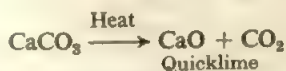


Chlorine is liberated at carbon anodes and stored to be used in the process:



The operation is continuous; magnesium chloride is fed in at the top as it is consumed. The molten magnesium metal, with a purity of 99.9%, is removed periodically and cast in ingots.

Aside from additions to make up losses in the process and the frequent replacement of the carbon anodes, the only raw materials required to produce magnesium are oyster shells,\* sea water and hydrogen gas. The slaked lime added to sea water to produce  $\text{Mg}(\text{OH})_2$  is made by calcining oyster shells ( $\text{CaCO}_3$ ):



and then adding water:



The chlorine liberated by electrolysis is burned with hydrogen gas to produce hydrogen chloride:



The hydrogen chloride dissolved in water is used to convert the hydroxide to magnesium chloride (Step 2). A flow sheet (Fig. 25.1) illustrates the steps in the production of magnesium metal.

Magnesium is the lightest of all structural metals. Its density is 1.74 g/ml,

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\* Huge mounds of shells are scooped up on the beach with earth-moving equipment for the process.

a third less dense than aluminum. It is a silver-white metal. Thin strips will burn when heated in an open flame in air. In fact, magnesium will burn in nitrogen, forming magnesium nitride (an intermediate in one of the preparations of ammonia already discussed). Because of its flammability it is

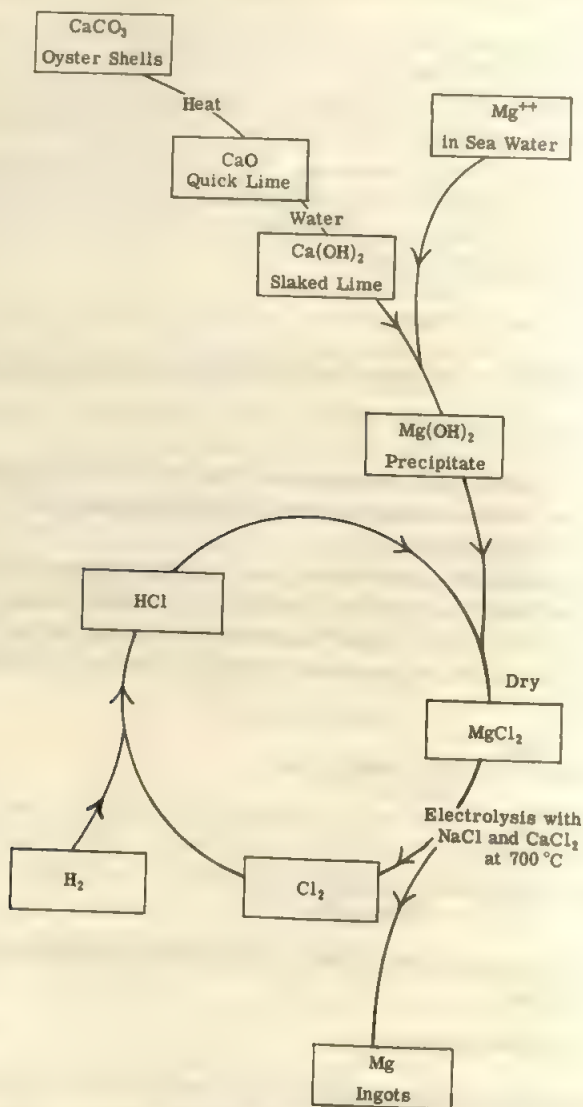


Figure 25.1. Flow sheet for the extraction of magnesium from sea water.

used in wartime in tracer bullets and in incendiaries. It is used as a "scavenger" in metallurgy. This will be mentioned later.

Pure magnesium is brittle and weak, but when alloyed with a small amount of aluminum, zinc or manganese it becomes strong, durable, machinable and

resistant to corrosion. The metal is used when light weight is necessary, especially in airplanes. During World War II, three hundred thousand tons were produced annually. Magnesium production is now in a recession; but in this air age, there is no doubt that new uses will be found for the light, durable, corrosion-resistant metal.

## B. ALUMINUM

Aluminum is a common metal now, but 100 years ago it was more costly than gold, despite the fact that aluminum is the most abundant metal in the earth's crust. Today the production of aluminum is second only to that of iron (1,450,000 tons in 1954). Despite its abundance, this would not have been possible were it not for a process developed independently in 1886 by an American, Charles M. Hall, and a Frenchman, P. L. T. Héroult, in which anhydrous  $\text{Al}_2\text{O}_3$  is electrolyzed (Step 4, below).

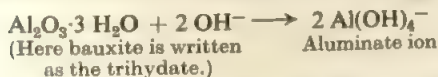
Aluminum occurs in many clays and rocks, but the sole source of commercial aluminum is the mineral bauxite. Bauxite, found in Georgia, Alabama, Tennessee, and Arkansas and in British and Dutch Guiana, is almost entirely hydrated aluminum oxide ( $\text{Al}_2\text{O}_3 \cdot X \text{H}_2\text{O}$ ) (where X is greater than 1 and less than 3), which contains impurities of ferric oxide, aluminum silicates and titanium dioxide.

The extraction and purification of aluminum follow the steps outlined in the flow sheet (Fig. 25.2).

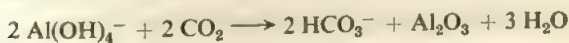
- (1) The bauxite ore is first crushed and ground to a very fine powder. It is then treated with a hot solution (about  $169^\circ\text{C}$ , under pressure) of sodium hydroxide made by adding sodium carbonate and calcium hydroxide. In solution sodium hydroxide is formed and insoluble calcium carbonate precipitates:



The basic solution dissolves the hydrated alumina from the inert material and other impurities



- (2) The clear solution containing sodium and aluminate ions is filtered from a "red mud" containing the impurities and allowed to cool in tanks into which carbon dioxide gas is bubbled. The carbon dioxide converts the aluminate ion back to  $\text{Al}_2\text{O}_3$ :



Lowering the temperature decreases the solubility of alumina greatly, and the trihydrate ( $\text{Al}_2\text{O}_3 \cdot 3 \text{H}_2\text{O}$ ) precipitates as large translucent crystals.

- (3) The crystals of hydrated alumina are washed, filtered, and then dehydrated as they pass through a large rotary kiln at  $1000^\circ\text{C}$ .
- (4) The white anhydrous powder is fed continuously into molten cryolite

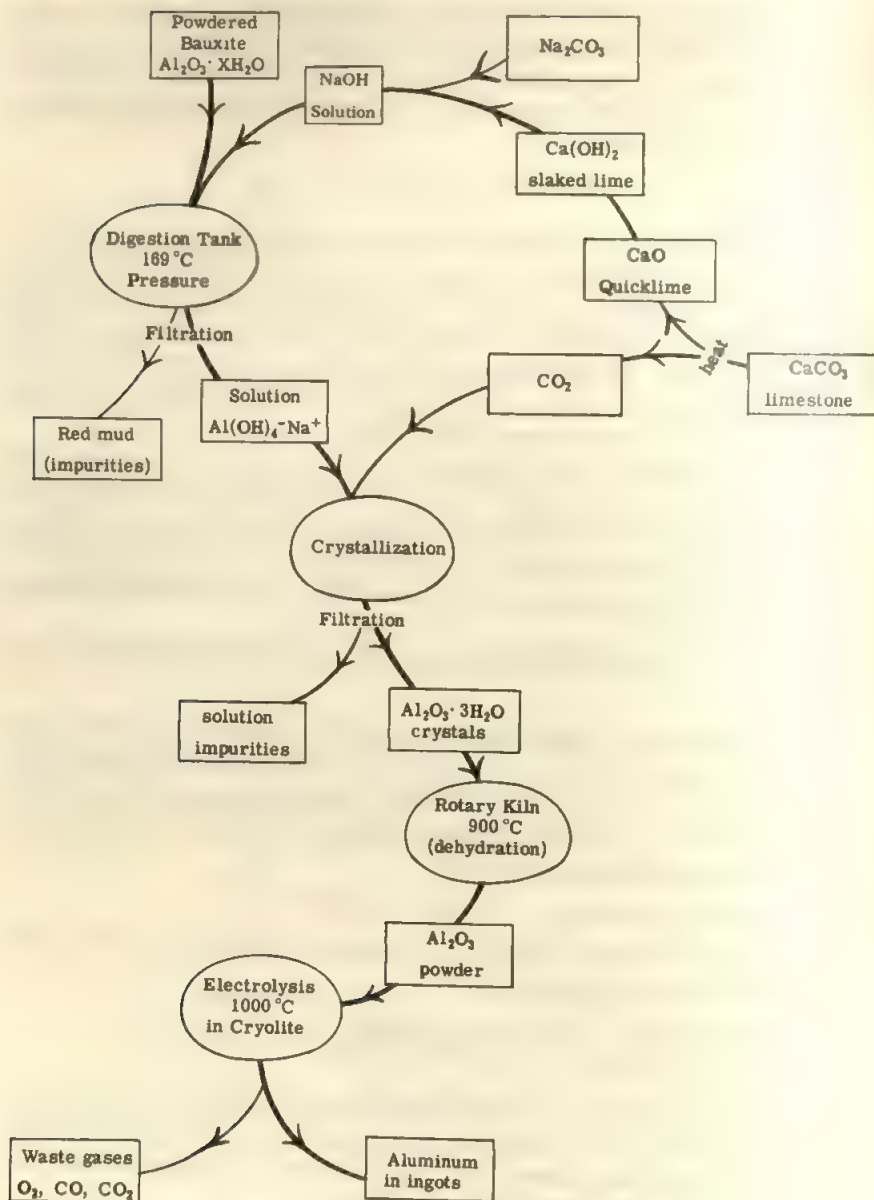


Figure 25.2. Flow sheet for the production of aluminum.

( $\text{Na}_3\text{AlF}_6$ ) at  $1000^\circ\text{C}$ , where it is electrolyzed. The electrolytic cell is a huge, carbon-lined steel container (about  $18' \times 8' \times 3'$ ) (Fig. 25.3).

The bottom lining is the cathode; aluminum is reduced at the cathode and collects as a molten pool to be drawn off periodically. Oxygen gas is liberated at the graphite anodes where it reacts with the



graphite, gradually consuming it to form carbon monoxide. The high temperature of the cell is maintained by the electrical resistance of the melt. Aluminum from the Hall process has a purity of about 99%. A great amount of electrical energy is required for this process. Each cell operates at about 50,000 amperes and at 6 volts. Aluminum plants must be located near cheap sources of electricity.

- (5) If aluminum of higher purity is desired, it may be refined by another electrolytic step, the Hoopes process. The aluminum to be purified is alloyed with copper to increase the density and is added molten to a cell at high temperature. A layer of fused cryolite, with barium fluoride

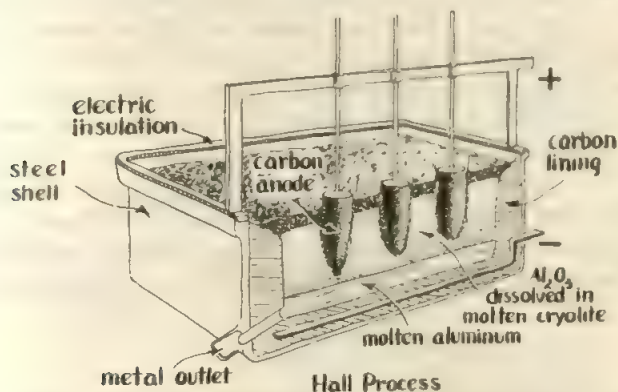
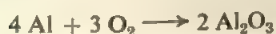


Figure 25.3.

added to increase the density, is placed on top. Above the cryolite layer is a pool of pure aluminum metal. The pure aluminum metal is the cathode; the impure aluminum alloy, the anode. Aluminum from the anode is oxidized and passes into the cryolite, while aluminum is reduced from the cryolite and collects with the cathode. Impurities are either left in the anode or accumulate in the cryolite layer. The purified aluminum is 99.99% pure.

Aluminum is a fairly active metal, as shown by its position in the electromotive force series. Powdered aluminum will explode when blown into air and ignited. Nevertheless, aluminum metal is resistant to atmospheric corrosion. Very pure aluminum is sufficiently resistant to be used as the outside coating of ocean-going vessels. Pure aluminum from the Hoopes process is coated over aluminum ship hulls. Aluminum's remarkable resistance to oxidation is deceiving. Actually the silver-white surface of newly cut aluminum "tarnishes" almost immediately on contact with air to form a thin almost transparent oxide film:



The film adheres tightly to the aluminum surface; no "buckling" occurs because the increase in weight is nearly compensated by an

increase in density of the oxide. The unbroken film prevents further oxidation. The higher the purity of the aluminum surface, the more closely the film adheres, and the more resistant the metal is to corrosion. If the metal surface is altered so that the oxide does not adhere, oxidation occurs. If mercury metal is rubbed on an aluminum surface to form a thin amalgam layer, the oxide does not adhere, and corrosion occurs rapidly.

The use of aluminum depends primarily upon its low density. With a density of 2.70 g/ml it is second only to magnesium. The soft, pure metal is not easily machined, but its alloys, made with small amounts of iron, magnesium, zinc, copper, silicon or manganese, are harder and can be machined. The tough alloys are used extensively in aircraft engines and bodies. Aluminum has high heat conductivity and is therefore used in cooking ware. The metal has good electrical conductivity. A copper wire of the same diameter has less electrical resistance than an aluminum wire. But an aluminum wire with the same weight per 100 feet is a better conductor than copper wire. Aluminum cable with a steel core for greater tensile strength is often used for electrical transmission cables. These are only a few of the uses. Aluminum roofs and so-called "tin-foil" candy wrappers are two of the many other uses.

### C. COPPER

The name copper is taken from the Latin word *cuprum*, which refers to the production of the metal on the island of Cyprus by the Romans. Copper has been produced from before the time of Christ. This is due in part to the fact that copper is sufficiently unreactive as to be found free or uncombined in many areas (the Lake Superior region, Arizona and New Mexico and the Mediterranean area). Rock containing native copper need merely be heated to the melting point of copper to separate the two. Copper occurs in extensive deposits as oxides or sulfides. The minerals are easily reduced to copper, also because of its lack of activity.

Although some high grade copper ore deposits are being mined and smelted, much of the world's copper is gained from low grade copper sulfide ores containing from 0.5 to 3% copper. The vastness of easily accessible deposits and a unique concentrating process combine to make the extraction economical.

- (1) *Mining.* Figure 25.4 illustrates the major steps in the extraction of copper from low grade ore. (The shaft mine is included to indicate that some copper ore is mined in that manner.) In the process to be described, the low grade copper ore is blasted from a mountainside in levels. The copper mine in Bingham Canyon, Utah, is a tremendous open pit hollowed-out of the walls and the bottom of a canyon. Ore is being taken from both the bottom and the sides of the pit. The walls are cut into steplike levels; each step is about 60 feet high and has a railroad track. Huge ore masses of about 50,000 tons are blasted with

ammonium nitrate from a 500-foot strip along the edge of a level. Ore running 0.4% copper or more is loaded into trains to be taken to the mill. Lower grade ore is loaded into other trains to be dumped elsewhere as waste. Blasting moves down from level to level, for blasting off one level widens the level below, until the 33 levels of the 2210-foot side of the pit have been moved back. When the circle at the mine

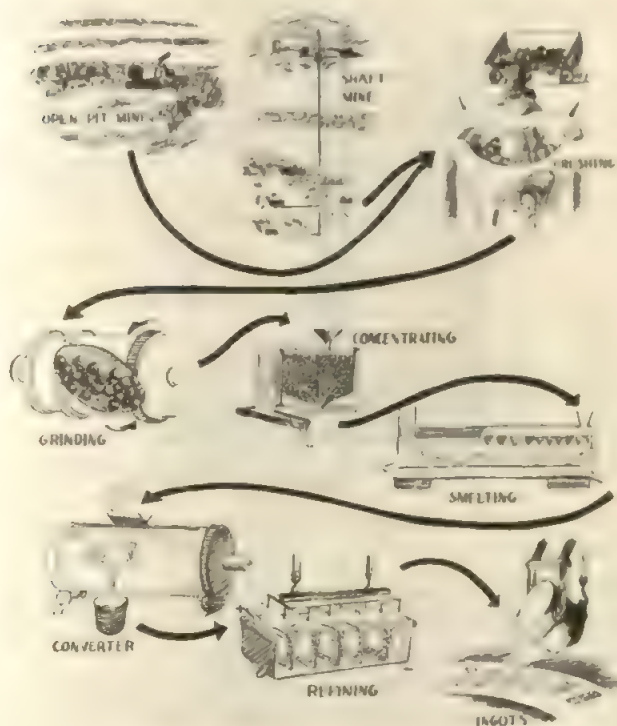
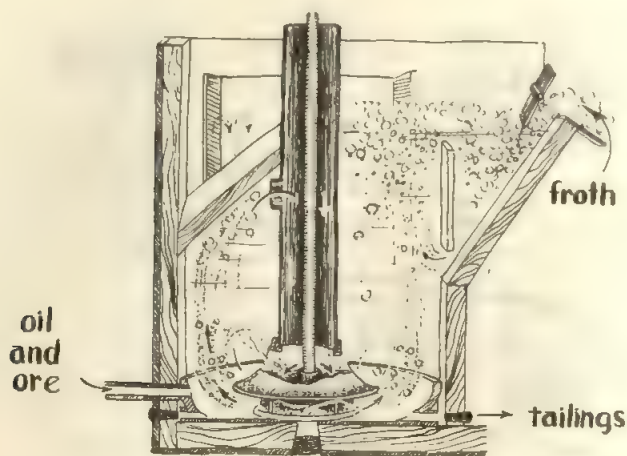


Figure 25.4. The metallurgy of copper.

bottom becomes of sufficient diameter for a track, the center is excavated and one more level joins the family of levels above. Approximately two-thirds of the material blasted is waste and is dumped.

- (2) *Concentration.* At the mills the ore cars are dumped into a giant gyratory crusher which can reduce granite boulders 3 feet in diameter to pieces not greater than 6 inches. The ore is further crushed and then ground in water in ball mills, where steel balls in a rolling steel barrel tumble over each other, powdering the ore that chances to be between, until 80 per cent of it will pass through a sieve with 10,000 openings per inch.
- (3) The fine ore in a water slurry is passed through a series of *flotation cells*, (Fig. 25.5). Here oil and a detergent are added, and the whole stirred.

The detergent is added to make bubbles with the oil. Oil is added to wet the mineral-bearing particles so that they rise with the bubbles as a froth on the water surface to spill over the side of the cell and collect in a large settling tank where the bubbles are burst in a spray of water to let the mineral settle to the bottom. The rock material bearing no mineral sinks and remains in the bottom of the flotation cell. After passing through several flotation cells, the rock materials are washed out as



### The Flotation Process

Figure 25.5. Flotation.

tailings on a huge dump. Only 4 pounds of each 100 pounds of ore entering the flotation cell are collected in the froth as concentrate. Ninety-six pounds are discarded as tailings.

- (3a) The product from the flotation process contains about 30 per cent copper. It may contain traces of other metals. At the Kennecott Copper Company mills, Magna, Utah, the concentrate contains 1.5 per cent molybdenite, and small traces of gold and silver. The molybdenite is worth separating. At those mills an additional flotation is carried out in the same type cells, but with a wetting agent or oil that wets the molybdenum-bearing mineral but not the copper mineral. Molybdenite is taken off as the concentrate and the copper concentrate remains as tailings.

The copper concentrate containing 30% copper in the compounds  $\text{Cu}_2\text{S}$  (chalcocite) and  $\text{CuFeS}_2$  (chalcopyrite) is filtered and dried ready for smelting.

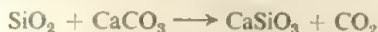
- (4) The first step in the smelting operation is a *roasting process*. The ore is heated strongly in the air. The sulfide is partially converted to the oxide. For cuprous sulfide the reaction is represented by this equation:





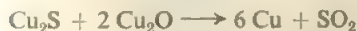
The sulfur dioxide gas is converted to sulfuric acid by either the lead chamber or the contact process.

The roasted ore is then *smelted* to remove the granite rock called gangue, represented as  $\text{SiO}_2$ . A flux, limestone ( $\text{CaCO}_3$ ), is added, which combines with the gangue to form slag, a low melting, glasslike compound:

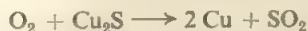


During the process both the slag and the copper sulfide copper oxide mixture are melted and run to the bottom of the furnace. The heavier copper-containing melt rests on the bottom. Periodically, as the molten slag and sulfide-oxide accumulate, they are run out, the slag to be dumped, the metal sulfide-oxide into forms in which it cools as ingots of copper matte.

The copper matte is finally reduced to copper in a converter, in which air is blown through the molten mass. The equations below represent the reactions taking place:



and



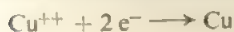
When conversion to copper is complete, the copper is cast into 700-pound slabs. The escaping of sulfur dioxide gas as the metal cools gives it a blistered appearance and the name of blister copper. Blister copper is about 99.5% copper.

- (5) Most copper is purified electrolytically and used for electrical wiring and electrical equipment. Impurities greatly reduce the conductivity. The presence of 0.03% arsenic reduces the conductivity by about 14%.

The refining takes place in huge electrolytic cells. Seven hundred pound blister copper anodes, about 3 feet square and 2 inches thick, are suspended in a copper sulfate solution between thin pure sheets of copper (cathodes) (Fig. 25.6). In the operation, copper is dissolved from the impure copper anodes:



while at the cathode the cupric ion is reduced to copper:



Copper is dissolved at the anode, transported as the cupric ion through the electrolyte and deposited on the cathode. As the anode grows thinner, the cathode grows thicker. Purification is accomplished because: (a) inert material and less reactive metals, such as gold and silver, are not ionized as easily as copper and are undermined by the dissolving copper and drop to the bottom of the cell as sludge. (b) more active metals present, such as iron, are ionized more readily than copper and dissolve in the solution, but are less readily reduced than copper ion and therefore remain in solution. The solution must be changed periodically.

Three hundred pound cathodes are removed from the cells every two weeks. One 700-pound anode makes two 300-pound cathodes. The scrap that remains is melted and recast into anodes.

The purified copper cathodes (99.9% copper) are melted in electric arc furnaces and cast in ingots of the shapes and sizes desired by manufacturers of copper wire and copper wares.

The sludge in the refining cells is collected very carefully to be treated for the extraction of silver and gold which were contained in the original

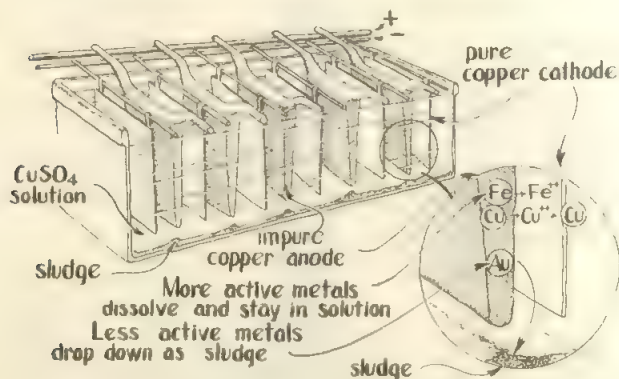


Figure 25.6. Electrolysis cell for the refining of copper.

ore in the proportions of 0.104 ounce and 0.017 ounce per ton respectively. Because silver and gold stay with the copper mineral, the complete metallurgical process serves to concentrate the precious metal in the sludge. At a price of \$35.00 an ounce, the value of the gold recovered is considerable.

Copper has a reddish brown color. (Copper and gold are the only common metals that have other than a silvery or gray appearance.) It has a density of 8.9 and a melting point of  $1083^\circ\text{C}$ . It is second only to silver in electrical conductivity, is resistant to corrosion (after formation of a thin oxide layer) and is much cheaper than silver. For these reasons, its chief use is in electrical wiring and in electrical appliances. It is a ready conductor of heat and consequently is used in and on cooking ware. It is also used in making coins, roofing, and water pipes.

Copper is used greatly in alloys. Some of these are bronze (copper, tin and zinc), brass (copper and zinc), aluminum bronze (aluminum and copper), and coinage silver (90% silver and 10% copper).

#### D. IRON

Iron is the most important of all metals. Iron and its alloy, steel, are literally the skeleton of the industrial structure. The reasons for iron's importance will be seen in the discussion to follow.

Iron was known in ancient times. The various ancient names meant "metal from heaven," indicating that iron was known as the free metal found in meteors. About 4.7 per cent of the earth's crust is iron. It is the second most abundant metal, second only to aluminum. It is believed that the center of the earth is molten iron. Like aluminum it is present everywhere in the earth's crust, but also like aluminum, at only relatively few spots is the extraction economical.

#### PRODUCTION OF IRON AND STEEL

Many factors are involved in choosing a site for a steel mill. Of prime importance is the availability of good iron ore. Iron does occur free in nature, but only to a limited extent. Minerals containing iron include hematite ( $\text{Fe}_2\text{O}_3$ ), magnetite ( $\text{Fe}_3\text{O}_4$ ), siderite ( $\text{FeCO}_3$ ), pyrite ( $\text{FeS}_2$ ) and chalcopyrite ( $\text{FeCuS}_2$ ). The two oxides are the principle minerals from which iron is made. Good deposits of siderite are not available, and sulfide ores are not used greatly, because the presence of even small traces of sulfur in iron or steel greatly affects the properties.

The physical state in which the mineral occurs affects its availability. The amount and kind of inert material, gangue, in the ore are important. The amount of gangue must be kept at a minimum and must be of such a composition as to be easily melted with the addition of a melting agent called flux. The expense involved in mining and the expense of transportation are other vital factors.

Not only are the state, availability and transportation of the iron ore important, but a source of good cokable coal is necessary, because coke is required in large quantities in the reduction process. Limestone must also be available, because limestone is the flux added to silica-bearing ore to convert the silica gangue to low melting calcium silicate slag. Water is not needed to produce iron, but it is required in great tonnages in the rolling of steel. All these must be available if a steel mill is to be successful. Approximately 2 tons of high grade iron ore, 0.5 tons of limestone, 1 ton of coal and 250 tons of water (used over and over) are required to produce 1 ton of steel.

The major steel-producing area of the United States is outlined on the map (Fig. 25.7). Steel-making centers are located largely in the Great Lakes area along the southern shores of Lake Michigan, Lake Erie and Lake Ontario. Economic conditions are met there.

The greatest iron deposits in the world are located in the Mesabi Range in northern Minnesota and Canada. The deposits are oxides, hematite and magnetite. Furthermore, the deposits have been raised during the geological history of the area; the covering has been washed off until the rich deposits lie very near the surface. Thin layers of earth have been removed to reveal great deposits of high grade ore. The ore is mined in the open and loaded into railroad cars. About 2 billion tons of high grade iron ore have been removed. Approximately 1 billion tons still remain. A much greater supply of low grade ore remains when the high grade ore is gone. The iron ore deposits are many miles from the steel mills. This disadvantage is offset by cheap water

transportation. Lake steamers carry the ore to the mills. It was thought once that the steel mills might shift to other areas. This appears less likely now because, with the opening of the St. Lawrence Seaway, the rich ores of Labrador and Venezuela may now be transported cheaply.

Great stores of anthracite coal lie in the mountains of Pennsylvania and West Virginia just south of the great steel area. Limestone deposits occur at the earth's surface in Ohio and Pennsylvania. The lakes and streams nearby contribute water.

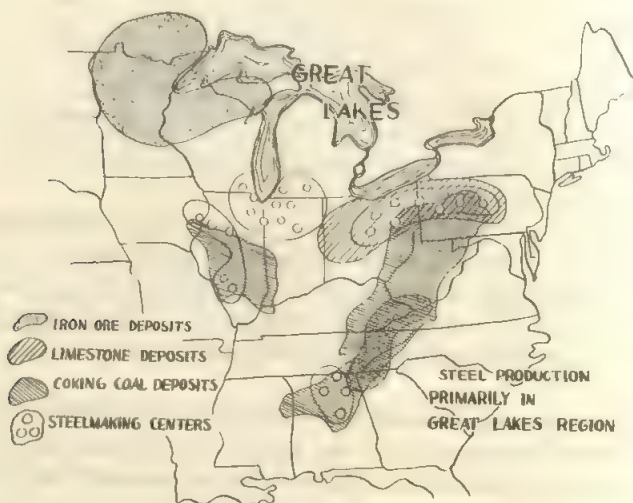


Figure 25.7.

Many iron ores are improved before smelting by one or more processes grouped under the title *beneficiation*. Beneficiation may constitute crushing and grinding the ore to allow the reducing gas to penetrate it more readily in the blast furnace. Or it may consist of roasting in air to remove sulfur by oxidation to sulfur dioxide or to convert the ore more completely to an oxide. One beneficiation process, mainly a concentration process, is important now that the depletion of high grade iron ores is a possibility. In this process, low grade hematite ore is crushed, ground, mixed with powdered coke and roasted. The roasting converts hematite to magnetite, a magnetic material, as the name suggests. The powder of coke and magnetite is then poured down through a magnetic field. The particles containing magnetite are deflected in the magnetic field and fall into a bin separate from the non-magnetic rock. The powdered concentrate may then be dumped into balling drums that roll powder into moist balls the size of walnuts. Finally the moist balls are hardened in the furnace for handling.

Iron is produced in the blast furnace, a hollow steel giant lined with fire brick (Fig. 25.8) and measuring about 100 feet high and 25 feet in diameter. The furnace operates continuously. Iron ore, coke and limestone are fed into



the furnace at the top. Preheated air from huge stoves is blown from the bottom up through the mixture of solids. Molten iron and molten slag are drawn periodically as they accumulate from the base of the furnace. The molten slag is dumped as waste; the molten iron is run into interconnected forms to cool.

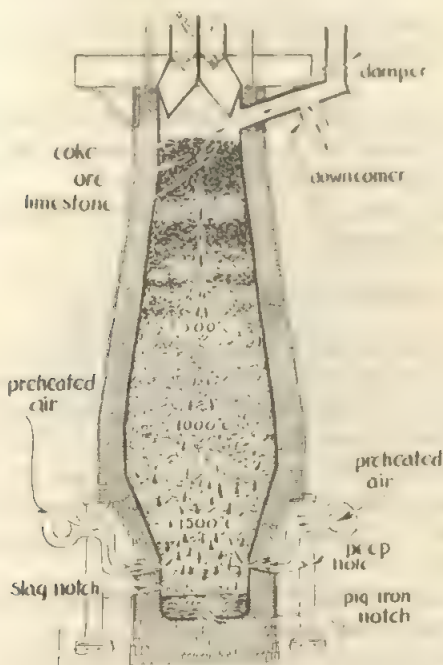


Figure 25.8. Blast furnace.

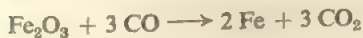
The reactions that occur to accomplish the conversion of ore to iron are probably many and complex and are not completely known. A plausible set of reactions is represented by the equations below:

- (1) Coke burns in the incoming air to form carbon monoxide.

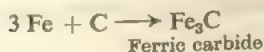


This reaction contributes the heat to maintain the furnace at the necessary temperature (about  $1600^\circ\text{C}$  at the hottest point).

- (2) Carbon monoxide (produced above) is the reducing agent. A gas, it can diffuse in and through the porous ore, where it reacts to produce iron.

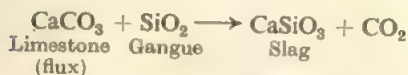


- (3) The iron reacts with unburned coke to form ferric carbide (which is 6.6% carbon).



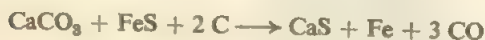
This reaction serves a purpose, because iron melts at  $1550^{\circ}\text{C}$ , whereas the melting point of iron carbide is  $1150^{\circ}\text{C}$ . Molten iron carbide then forms a considerable distance up inside the furnace and runs down to collect in the base.

- (4) Removal of the inert rock material (gangue) is made easier by this reaction:



Not only does slag have a lower melting point than gangue, but it runs nicely down through the charge, whereas molten silica tends to form a sticky layer over the walls and the charge.

- (5) Coke and limestone assist in removing other impurities combined with the iron, such as sulfur:



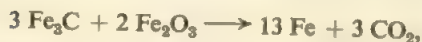
The calcium sulfide melts and runs to the furnace base where it is dissolved in the slag layer above the molten iron carbide.

After cooling, the impure iron (mostly ferric carbide) is dumped from the interconnected mold and broken apart. These chunks of metal were thought by some to look like pigs, hence the product from the blast furnace is called "pig iron." While the metal pigs cool in the forms, a thin layer of slag rises to form over them and protect them from oxidation.

It takes about 12 hours for material added at the top to pass through the blast furnace and come out as iron and slag. Nevertheless, one blast furnace often produces 1,000 tons of pig iron per day.

Pig iron is 92 to 94% iron with carbon, slag and other impurities. It may be used as it is for some purposes. Pig iron that is poured into a mold and allowed to cool rapidly forms a very hard shiny gray material called white cast iron, largely a solid solution of carbon in iron. When a casting of pig iron is allowed to cool slowly, a hard black material is formed, called black cast iron. Black cast iron is largely ferric carbide crystals with flakes of carbon. Both are very brittle. In the past, soil pipes, old iron stoves and certain locomotive parts were made of cast iron. Now tougher steel has almost entirely replaced cast iron.

Wrought iron was made by puddling pig iron and iron oxide. Puddling amounts to prolonged stirring of the molten mixture. Carbon is burned from the cast iron:



until the iron contains 0.01 to 0.02% carbon and slag fibers. Wrought iron is soft and malleable. The slag prevents oxidation. Anvils, chains, anchors and wire were once made of wrought iron; now they are made of low carbon steel.

## E. STEEL

Almost all iron used in industry is in the form of steel, which is an alloy. Ordinary steel is iron alloyed with from 0.2% to 1.5% carbon. So-called alloy steels contain iron with a small percentage of such substances as cobalt, vanadium, chromium, tungsten and silicon.

Steel is made from pig iron by (1) removing impurities, (2) adding definite amounts of either carbon or another element or elements and (3) administering such heat and rolling treatments as are needed for the properties desired.

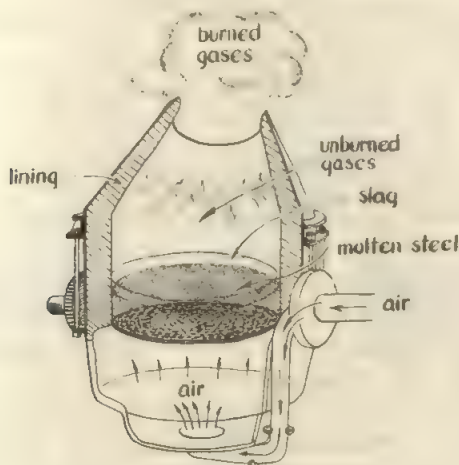
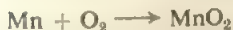
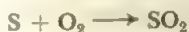


Figure 25.9. The Bessemer converter.

The steel rails that spanned the continent in 1869 were made from steel made in a *Bessemer converter*. The Bessemer converter of today is a huge oval shaped barrel (Fig. 25.9) that may be tipped to accept molten raw iron from the blast furnace and to dump the steel when it is finished. The converter is loaded with 15 to 20 tons of molten pig iron. A blast of air forced up through holes in a false bottom burns out impurities.



The last reaction is the major reaction. The gases formed escape in the flame. Solid oxides combine with the converter lining to make slag, which rises to the top. The blast of air with a great flame continues for about 10 to 15 minutes. When the impurities have been burned, as determined by the color of the flame, the air is turned off. Either carbon (usually as spiegeleisen, a high carbon steel) or other alloying agent is added and the contents are dumped into a ladle to be cast into ingots for the required further treatment. However, this method, which is the quickest method of making steel.

has an inherent weakness. Analysis by flame color is not thoroughly reliable, and there is insufficient time for chemical analysis. Some batches of steel are excellent; others are poor.

Less than ten per cent of the steel produced today is produced in the Bessemer converter. Ninety per cent is prepared in the open hearth furnace. The open hearth furnace is a great steel tray with a thick lining of calcium oxide fire brick (Fig. 25.10). Pig iron (raw iron) from the blast furnace, rusted scrap

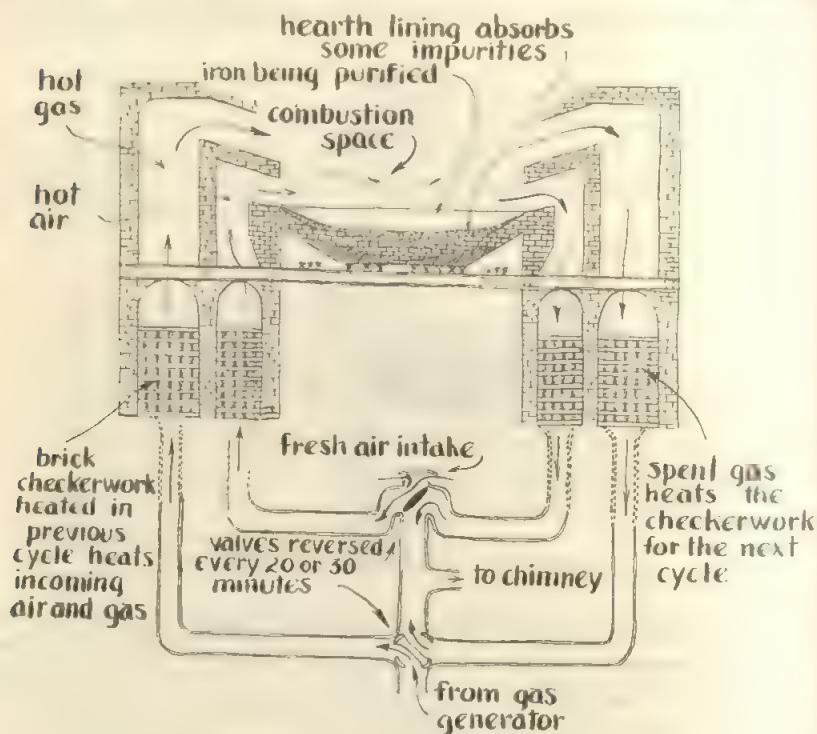
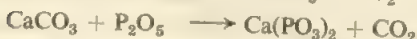
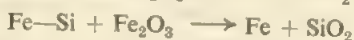
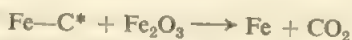


Figure 25.10. Open hearth furnace.

iron, pure hematite ore ( $\text{Fe}_2\text{O}_3$ ), coke and a small proportion of limestone are placed in the tray, which may hold 150 tons. The whole is heated by burning a preheated mixture of air and natural gas.

Some of the reactions occurring in the melt are represented by these equations:



\*  $\text{Fe}-\text{C}$  is used to represent an alloy of no definite proportions of iron and carbon. Because the proportion is not definite, the equation is not balanced.



Samples are taken from the seething white hot mass (about 1600°C) at intervals and analyzed. When the composition is just right for the steel desired, usually after 9 to 12 hours, the molten steel is discharged into ladles to be cast into ingots. During the heating in the furnace, materials may be added to the charge as required. Just before dumping, a trace of magnesium metal or other active metal is added as a "scavenger." A scavenger merely combines with any dissolved oxygen that escapes during cooling, remains in the steel as an oxide, but prevents formation of oxygen bubbles in the steel. Figure 25.10 attempts to show how the burning gases that have passed over the hearth charge are passed through extensive brick work, heating it to a high temperature. The flow of gas and air is then reversed, and the gas mixture derives heat from the bricks as the bricks on the opposite side are being heated. Much heat is conserved by this arrangement.

For many structural purposes, the ingots stripped from their molds are carried to soaking pits, which are great gas-heated furnaces maintained at about 1200°C, somewhat below the melting point of the steel. The ingot is left there for the necessary time (perhaps 24 hours) until heated all the way through to the pit temperature. The ingot is then transferred to rolling stands where it passes between huge, water-cooled rollers, by which it is reduced to slabs, plate, steel sheet or rods. Two hundred and fifty tons of water passes over each ton of steel in rolling. Not only does the rolling reduce the metal to the desired thickness, but it toughens it. The major steps in the production of steel are illustrated in Figure 25.11 (pp. 414 and 415).

Certain steels receive special treatment to gain desired properties. Hardness and brittleness increase with the increase of carbon. Following are the approximate percentages of carbon in three grades of steel.

0.2% C or less	mild steel (wire, chains, anvils, etc.)
0.2 to 0.6% C	medium steel (structural steel)
0.6 to 1.5% C	high carbon steel (cutting tools, razor blades)

The greater the amount of carbon, the greater the amount of ferric carbide with its hard, brittle crystals.

Heat treatment affects the properties of steel to a remarkable degree. This is possible because there are two allotropic forms of iron. Alpha iron is stable between the melting point (1535°C) and 1400°C and also below 906°C. Gamma iron is stable between 906°C and 1400°C. Furthermore, carbon and iron form compounds with different forms and may form solid solutions. Very rapid cooling from high temperature leaves the steel mostly in the more brittle gamma form, for changes from one form to another in the solid are slow at high temperature and essentially nil at room temperature. Cooling more slowly to 800°C and then quenching leaves the metal partially in the alpha form, whereas very slow cooling gives a still higher percentage of alpha iron.

A wide range of properties may be given "quenched" steel (that is, steel that is cooled very rapidly by immersing it in water, oil, or even liquid mercury) by further heat treatment. The metal may be merely heated to a temperature

much lower than the melting point, then allowed to cool slowly. Table 25.2 illustrates the change in use occasioned by change in properties of quenched high carbon steel that is reheated to various temperatures.

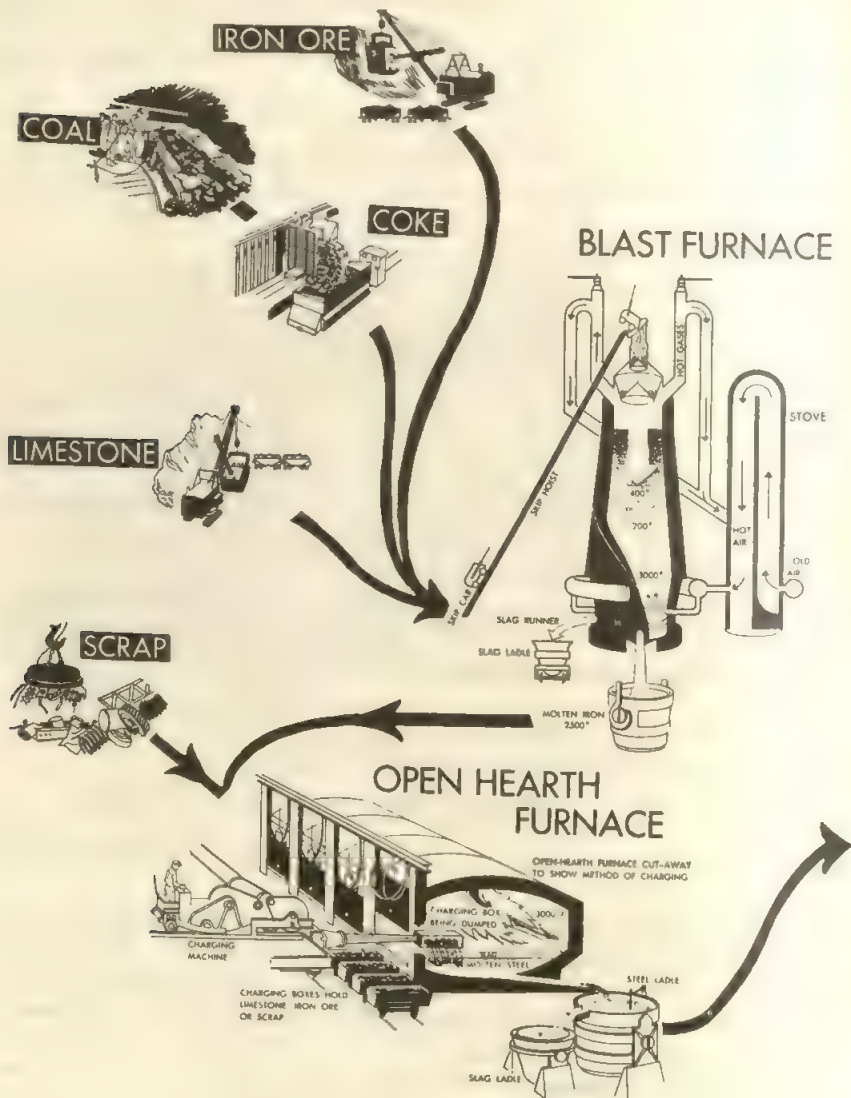


Figure 25.11a. Metallurgy of steel. \*

\* All temperatures are in °F.

The data are relative, but they do indicate that the higher the temperature is raised (even though it is much lower than the melting point) and allowed to cool slowly, the more steel is converted to the softer forms.

A steel that is both tough and hard—tough like medium carbon steel,

and hard like high carbon steel—is sometimes sought. An axle needs these properties; it must be hard for a bearing surface, but tough so it will not break with a sudden jar. These qualities may be achieved by placing a medium

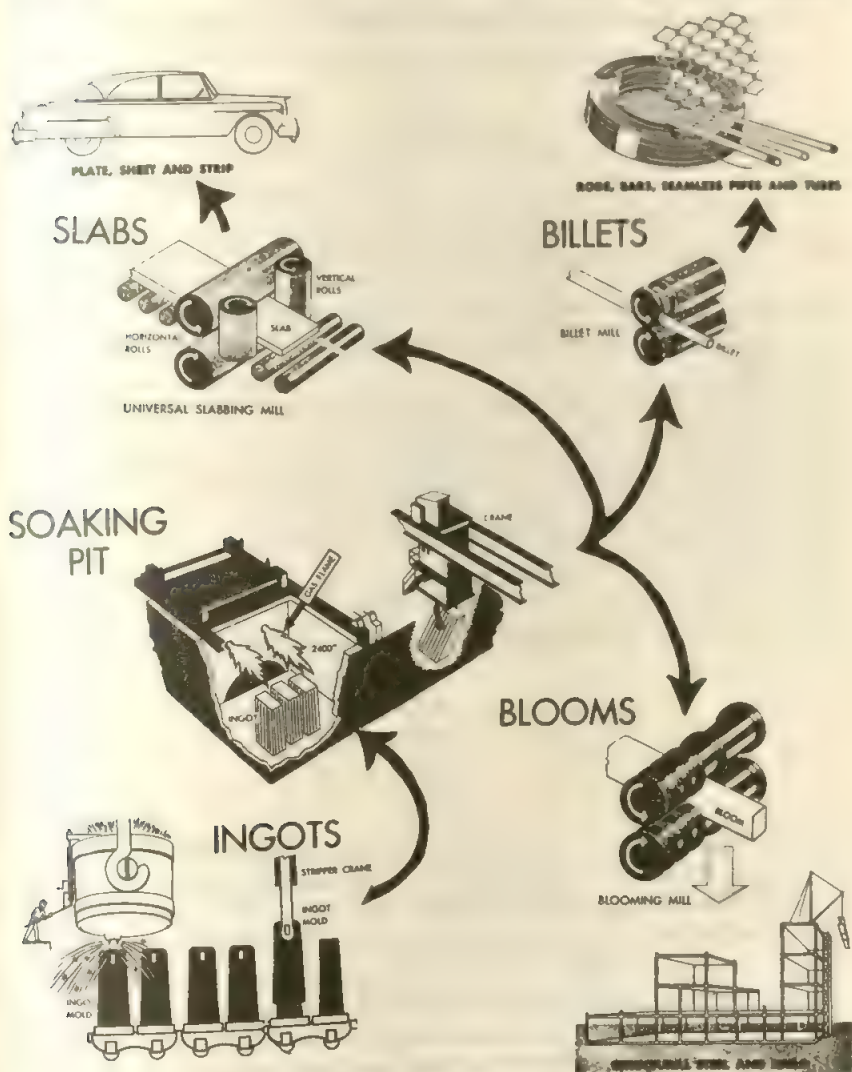


Figure 25.11b. Metallurgy of steel. \*

\*All temperatures are in °F.

(Courtesy of United States Steel Corporation)

steel rod surrounded by powdered carbon in a furnace, and then heating it rapidly. When the outside of the rod becomes hot, it reacts with the carbon. The colder and less accessible metal inside does not. Upon cooling, a sheath of high carbon steel surrounds medium steel. The process is called case-hardening.

So-called *alloy steels* are made by adding another element besides, or in place of, carbon. A wide variety of properties can be given steel by changing the alloying components. Some interesting alloys with approximate properties and compositions are:

- (a) *Stainless steel* (18 % chromium, 8 % nickel, 74 % iron) is very resistant to corrosion and remains bright and shiny.
- (b) *Cobalt steel* (a small per cent of cobalt) is hard, resistant to corrosion, and maintains its physical properties at high temperatures. It is used for high-speed cutting tools and surgical instruments.
- (c) *Manganese steel* (12 to 14 % manganese) is extraordinarily hard. Crushing machines and safes are made of it.
- (d) *Chromium-vanadium steel* (5 to 10 % chromium; 0.15 % vanadium) is tough and elastic. It is used for automobile axles and frames.
- (e) *Tungsten steel* is used in armor plate and metal-piercing shells. Tools containing as much as 20 % tungsten hold a cutting edge even at red heat.
- (f) *Silicon steel* (1 to 2 % silicon) is hard and strong; steel containing 12 to 15 % silicon is resistant to corrosion.
- (g) *Molybdenum steel* (6 to 7 % molybdenum) holds its temper when heated.
- (h) *Lead steel* (0.02 % lead) is easily machined.
- (i) *Titanium steel* (0.1 % titanium) is very hard.

**Table 25.2.**

230°C	razor blades
250°C	pocket knives
260°C	scissors and chisels
270°C	butcher knives
290°C	watch springs
320°C	saws

These are only a few of the elements and a few of the percentages used in steel alloys. Other elements used are: cesium, copper, niobium, zirconium, hafnium, tantalum, nitrogen, phosphorus and sulfur. They are the transition metals and the non-metals of Groups IV, V and VI of the Periodic Table.

The above is but a brief and non-technical discussion of steel. It is estimated that an average of 30 pounds of other elements are found in each ton of steel. A steel may contain as many as five or six different elements. By judicious use of alloying agents, heat treatment and handling (such as hot or cold rolling), steels with an infinite variation of properties are made. For this reason and also because of its accessibility, iron is the most important of all industrial metals. More iron (steel) is produced than all other metals combined.

The one property of steel that cannot be varied greatly by alloying is the density. Iron has a density of 7.86 g/cm<sup>3</sup>. It is a silver-colored metal and is not especially resistant to corrosion. Pure iron cooled slowly is quite soft. All these properties except density can be changed by alloying or some other

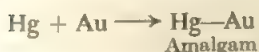


treatment. Industry will see the gradual further displacement of steel by aluminum and magnesium in areas where light weight is at a premium. This substitution will be more pronounced as available high grade iron ore supplies dwindle. Eventually plastics will displace steel in many uses. Today however, a country's might may be measured by the amount of steel it produces. The United States produces about 40 per cent of the world's steel.

## F. SILVER AND GOLD

Silver and gold are classed together in this discussion because: (1) both occur as the free metal in nature, (2) the metallurgy of the two metals is very similar and (3) they often occur and are gained from nature together. Three processes will be mentioned briefly.

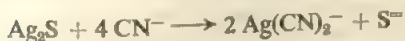
- (1) The first is a very simple *flotation*, known better as panning. Gold- or silver-bearing sand is washed very carefully from a shallow pan. The heavier metal particles (gold,  $19.6 \text{ g/cm}^3$ , and silver,  $10.5 \text{ g/cm}^3$ ) remain in the bottom of the pan. Sluice boxes are a more efficient method of "panning." The sand in water flows down the floor of a long wooden box with transverse cleats. The metal particles collect at the front edge of each cleat while the sand is swept over.
- (2) A sluice box can be made much more effective if mercury metal is placed in the box so that little pools of mercury are present at the upper edge of each cleat. Even the tiniest particles of either gold or silver dissolve in the mercury to form an amalgam (mercury alloy), represented by the equations:



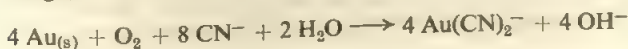
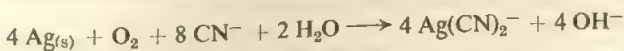
The mercury solution is changed from time to time and the mercury distilled to leave the precious metals behind.

- (3) The *silver cyanide method* is still more effective than amalgamation in recovering the metals. It is a chemical method and recovers even the silver that occurs chemically combined in nature.

To the pulverized ore in large vats is added a solution of sodium cyanide; the mixture is allowed to stand several days. Any horn silver ( $\text{AgCl}$ ) or silver sulfide present dissolves readily to form a complex ion:



More time is required for air oxidation of the native gold or silver:



The precious metals are then obtained by adding zinc, which displaces them in the complex ion:



and



Silver and gold precipitate on the surface of the dissolving zinc. Silver is separated from the gold by dissolving in nitric acid. Tailings from old silver mines are being reworked by the amalgamation and sodium cyanide processes. The gold- and silver-bearing sludge from the electrolytic refining of copper is treated by the sodium cyanide process.

Much silver occurs in lead ores. Silver stays with the lead throughout the milling and smelting and is therefore present in the molten lead as it issues from the furnace. It so happens that silver is much more soluble in molten zinc than in lead, and that lead and zinc are insoluble in each other. Extraction of the silver by the Parkes process is based on these facts. About 2 per cent zinc is added with agitation to the molten, silver-bearing lead. When agitation ceases, the lighter zinc collects as a layer on top with most of the silver. The zinc layer freezes first as the metal cools and is broken up and removed before the lead solidifies. Zinc and silver are then separated by distilling the zinc.

The appearances of silver and gold are well known. The pure metals are too soft for use except in alloys. Silver is used in coins (90% silver and 10% copper). Silver is the best reflector of visible light and is used as mirror backing. It is the best electrical conductor, but the price limits its use in electrical appliances.

Silver and gold alloys are used in jewelry. Yellow gold is a gold-copper alloy. White gold may contain either platinum or nickel. The proportion of gold in jewelry metal is often given in "karats." The karat rating is the parts gold by weight in 24 total parts. 24K gold is pure gold. 14K gold is 14/24 gold by weight, the remaining 10/24 part is copper or another metal.

Gold is the most malleable and ductile of all metals. It can be beaten into leaves so thin that they are transparent (0.00001 mm). One cubic centimeter of gold of that thickness would cover one-fourth acre. Gold can be drawn into a thread so fine that 1 cubic centimeter of it would be 24 miles long.

## EXERCISES

1. List 10 common metals.
2. Where are the common metals in the Periodic Table?
3. Are the common metals the most active metals? Explain.
4. What is the major source of magnesium for commercial uses?
5. What other raw materials besides sea water are used in the production of magnesium?
6. What happens to the chlorine gas released in the electrolytic reduction of magnesium chloride?
7. What is the purity of magnesium produced by electrolysis?
8. Define metallurgy.
9. What property dictates the use of magnesium in the aircraft industry?
10. How is aluminum separated from the rock and iron oxide in the ore?

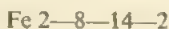
11. Describe the Hall process. What purpose does cryolite serve?
12. Describe the Hoopes process.
13. What protects the active metal aluminum from rapid atmospheric corrosion?
14. In what industry does aluminum find its major use?
15. How does aluminum compare with copper as an electrical conductor?
16. Which of these metals occurs free in nature: iron, copper, magnesium, aluminum, silver or gold?
17. Describe the concentration (flotation) process for low grade copper ores.
18. How is molybdenite separated from the copper concentrate?
19. Describe the three processes in copper metallurgy for which heat is required. Write the equations. Define the terms: blister copper, copper matte, flux, slag and gangue.
20. How is blister copper purified? What happens to the more active metals present? What happens to the less active metals?
21. List four uses of copper metal.
22. What raw materials are needed to produce steel?
23. Which four "common" metals are most abundant in the earth's crust? (See Table 11.3.)
24. Name two useful iron ores and write their formulas.
25. Write five equations for processes occurring in the blast furnace.
26. Why is the steel center of America located on the shores of the Great Lakes?
27. Describe one concentration process for low grade iron ore.
28. What is pig iron? Where is it produced? What is its composition?
29. Describe three functions of coke in the blast furnace.
30. What is cast iron?
31. Define steel.
32. What are the three major operations in converting pig iron to steel?
33. Why is *rusty* scrap iron added to the open hearth charge?
34. How may one vary the properties of steel with a set percentage of carbon.
35. Write the approximate composition of stainless steel.
36. Describe three methods for recovering finely divided gold dust from sand.
37. Which common metal is the best electrical conductor?
38. Which metal is the best reflector of visible light?
39. Which metal is the lightest of all "common" metals?
40. Which metal is the most ductile and malleable?

CHEMISTRY OF THE  
COMMON METALS

## 1. REVIEW

A considerable amount of the chemistry of common metals has been discussed in previous chapters in connection with other topics.

A. In the discussion on bonding (Chapter 7) it was noted that the transition elements tended to *lose electrons in reactions* and therefore are metals from a chemical standpoint. It was pointed out that the transition metals may exhibit *two or three different ionic valences*. Owing to the instability of an underlying electron structure (the number of electrons in the next outermost level being other than 8), some of these electrons may or may not be lost in bonding. The element iron (at. no. 26) was cited as an example. The atom has this structure:



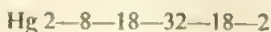
The ferrous ion has the structure:



and the ferric ion this structure:

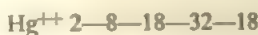


It is obvious that, in addition to the two in the outermost shell, one more electron has been lost in the formation of the ferric ion. The ferric ion appears to be as stable as the ferrous ion, since there are more ferric than ferrous compounds. Other examples are: cuprous ( $\text{Cu}^+$ ) and cupric ( $\text{Cu}^{++}$ ); cobaltous ( $\text{Co}^{++}$ ) and cobaltic ( $\text{Co}^{+++}$ ); chromous ( $\text{Cr}^{++}$ ) and chromic ( $\text{Cr}^{+++}$ ). Mercurous and mercuric are not quite analogous, for the structure of the mercury atom is:

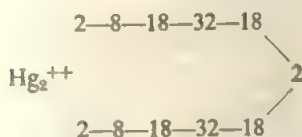




The structure of the mercuric ion is:

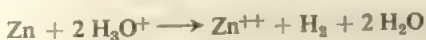


but the mercurous ion is a "complex ion" (that is, it has more than two atoms) that might be represented as follows:



The mercuric ion has lost the two valence electrons, whereas each of the two atoms in the mercurous ion have lost one and have contributed the remaining valence electron to a pair shared between them.

B. One important reaction of these metals—the *displacement of the hydronium ion* from an acid solution—was discussed with the chemistry of hydrogen. For zinc metal the reaction is:



The common metals were arranged with the active metals (in the electromotive force series) in the order of the ease with which they replace hydrogen. Related reactions, the *displacement of one metal from solution by another*, were discussed at that time. The order with which they replace one another was shown to agree with the electromotive force series. For example, copper displaces the silver ion:



These reactions were discussed further in Chapter 17 in the discussion of primary cells. The electrode voltages found in the electromotive force tables were used for the quantitative determination of the voltage of a cell in which these reactions take place.

Finally, some chemistry has appeared in the metallurgical processes discussed in the previous chapter. It is not our purpose in this chapter to repeat that chemistry, but to refer to it when necessary to assist in understanding an important branch of structural chemistry that finds greatest expression among metal-centered complex ions.

## 2. METAL-CENTERED COMPLEX IONS

The making of black and white photographs is a chemical process. A photographic film is a plastic strip coated with an emulsion (a gel) in which are imbedded minute silver bromide crystals (Fig. 26.1a). When the film is

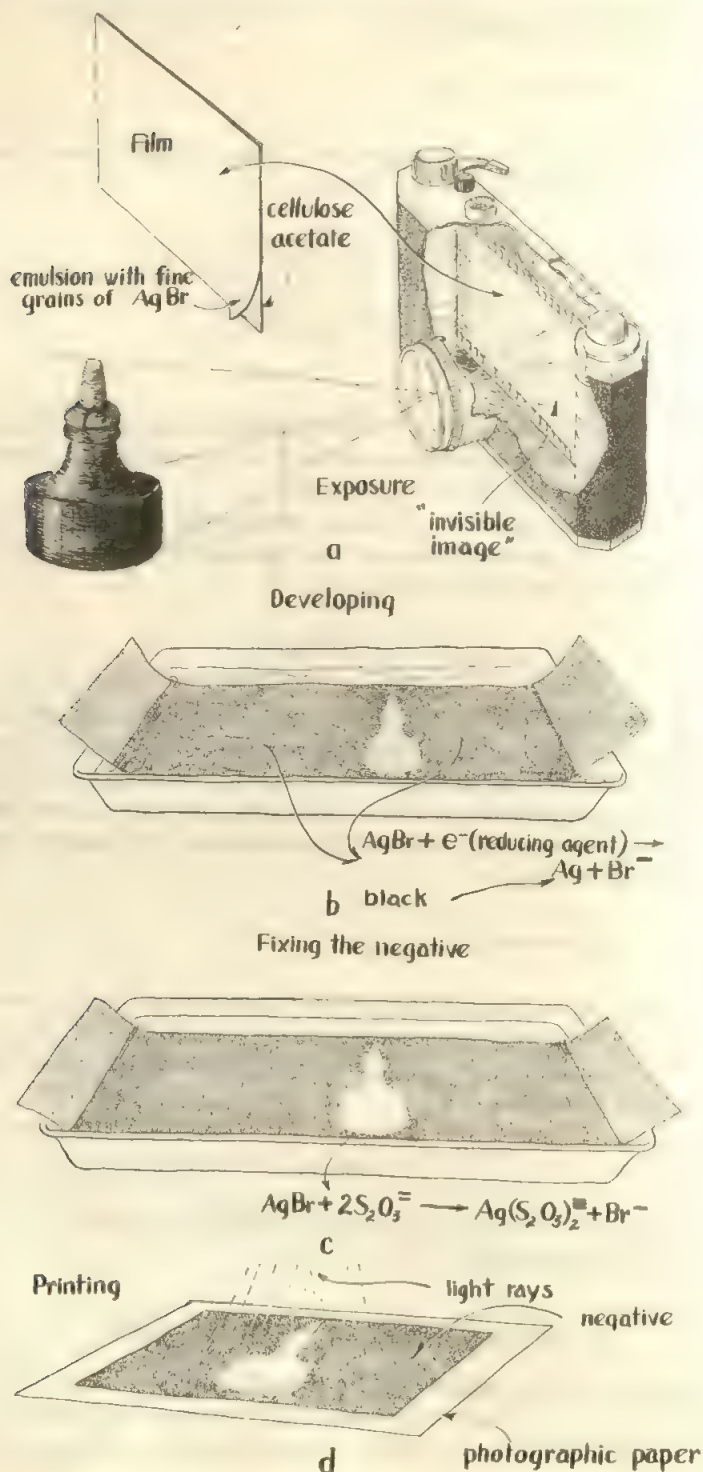


Figure 26.1. Black and white photography.

exposed (the picture is taken), light reflected from light-colored and white objects passes through the lens and falls on the emulsion. The incidence of light breaks down the physical structure of the silver bromide crystals so that they are more susceptible to chemical attack. The emulsion must be kept in the dark except for the exposure. After exposure the film is removed from the camera and in a dark room is developed in a solution of a reducing agent (Fig. 26.1b). The reducing agent reduces the silver ion in silver bromide crystals to silver, which in a finely divided state is black. The imperfect (exposed) particles of silver bromide are reduced much faster than the unexposed particles. (However, all the silver bromide particles would be reduced if left in the developing solution too long.) The darkening, or developing, is stopped by washing the film in water and then in a "fixing" solution (Fig. 26.1c). The fixing solution, sometimes called "hypo," is sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ ). Washing in sodium thiosulfate removes the unreduced silver bromide, which is dissolved by the formation of a very stable complex ion:



The ions in solution are washed from the film. When dried, the treated film is a finished negative, on which white objects appear black, black transparent and gray remains gray—for where light struck the film, black silver remains. The making of the positive, the photograph, follows the same steps of exposure, developing and fixing. Photographic paper (paper with a silver bromide-containing emulsion) is exposed to the light through the film (Fig. 26.1d). When developed and fixed, a positive is obtained, appearing white where the film was dark and black where the film was transparent.

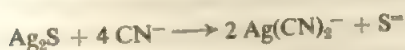
The fixing step, the formation of the complex ion that can be removed by washing, is of interest here. It is a combination of  $\text{Ag}^+$  and  $2 \text{S}_2\text{O}_3^{2-}$  and should have a charge of minus 3, which it does:  $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ .

There are other complex ions of silver:

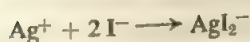
- (a) Silver chloride dissolves when ammonia solution is added (Chapter 23) and the silver ammonia complex ion is formed:



- (b) Silver is dissolved from silver sulfide-containing ores in a sodium cyanide solution (Chapter 25):



- (c) Although silver iodide precipitates quantitatively from a dilute potassium iodide solution to which silver nitrate solution is added, it does not form in a concentrated iodide solution. Again a complex ion is formed to keep the silver and iodine in solution.

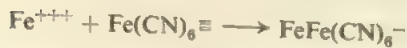
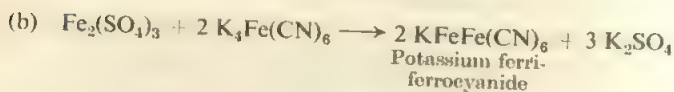
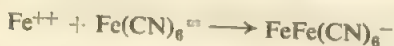
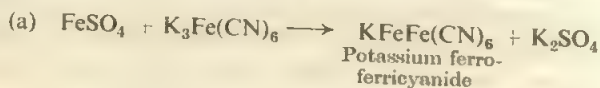


Silver is not the only metal found in complex ions. The metals found in Table 26.1 (a portion of the Periodic Table) and chromium form complex ions with ammonia. Some of these are:  $\text{Ni}(\text{NH}_3)_4^{++}$ ,  $\text{Cu}(\text{NH}_3)_4^{++}$ ,  $\text{Co}(\text{NH}_3)_6^{+++}$  and  $\text{Pt}(\text{NH}_3)_4^{++}$ .

Table 26.1. Elements Forming Ammonia Complexes

Cr 24 and			
27 Co	28 Ni	29 Cu	30 Zn
45 Rh	46 Pd	47 Ag	48 Cd
77 Ir	78 Pt		80 Hg

Although iron is not one of the metals that form metal ammonia ions, both ferric and ferrous ions form many complexes. Among these are 2 very similar ions, ferrocyanide and ferricyanide. They are found in analogous compounds, such as potassium ferrocyanide ( $\text{K}_4\text{Fe}(\text{CN})_6$ ), a lemon yellow solid, and potassium ferricyanide ( $\text{K}_3\text{Fe}(\text{CN})_6$ ), a reddish orange solid. An additional complex ion can be formed either by adding ferrous ion to ferricyanide in solution or by adding ferric ion to ferrocyanide in solution.



At one time it was thought that these identical compounds were different. They carried different names, Turnbull's blue and Prussian blue. Prussian blue is one of two inorganic pigments with the most intense color. The formation of this blue pigment is involved in "blueprinting." Blueprints appear as white lines on a blue background. Blueprint paper has been soaked in a solution containing potassium ferricyanide and ferric ammonium citrate. "Inked" plans on thin paper are laid over the dry blueprint paper in a dark room. Light passes through the drawing, except where structural lines or lettering appear, and activates the reduction of ferricyanide to ferrocyanide by the citrate ion. Placing the exposed paper in water allows the ferric ions and ferrocyanide ions to combine to form the blue pigment. The unexposed



salts are washed away, leaving white lines and lettering. The ferriferrocyanide ion is unstable in basic solutions. One can write white on blue prints with sodium carbonate ink.

### A. THE NATURE OF BONDING IN METAL-CENTERED COMPLEX IONS

X-ray studies show that these complex ions are metal-centered. The configurations of some are shown in Figure 26.2.

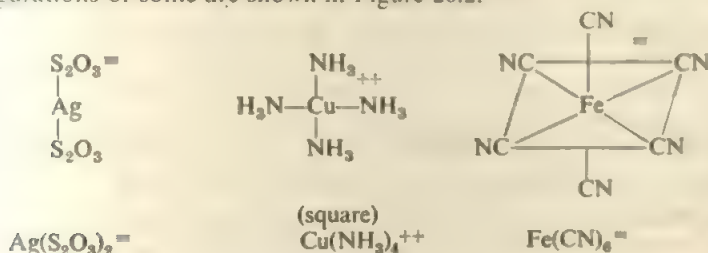


Figure 26.2. Configurations of some complex ions.

The bonding is covalent; the ions or molecules complexing with the metal must supply the electrons, and must therefore contain unshared pairs. Some coordinating groups are listed in Table 26.2.

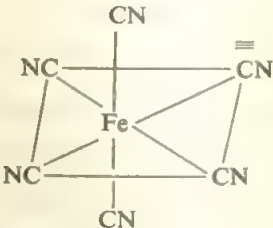
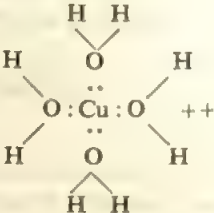
The following conditions favor the formation of these covalent bonds and hence the formation of complex ions:

- (1) A high charge on either the metal ion or the complexing group; the two fragments must be attracted strongly to one another or no bond results.
- (2) The metal ion should be small. The smaller the metal ion, the closer the coordinating group can approach, and therefore the tighter the donated electrons can be held. The many charges (more than 8) attracting electrons in the "outer" shell of transition metal ions tend to keep the ions small.
- (3) A large complexing group complexes more readily. The larger the group, or more correctly, the larger the shell which holds the electron pair to be donated, the more easily the electrons are "drawn out" for sharing.
- (4) Metal ions whose "new outer shell" has more than 8 electrons complex more readily than those with an inert gas structure. Calcium, magnesium and aluminum form complex ions, but not so readily as the transition elements, because they tend not to accept electron pairs to increase the outermost electron number above 8.

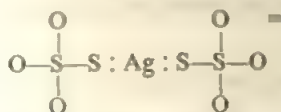
### B. THE COORDINATION NUMBER OF METALS IN METAL-CENTERED COMPLEX IONS

The coordination number of a metal ion is defined as the number of donated pairs of electrons it shares with complexing groups. For all silver

Table 26.2. Some Coordinating Groups

Group		Example
$\begin{array}{c} \cdot\cdot \\ :\text{Cl}: \\ \cdot\cdot \end{array}^-$ Chloride ion	$\text{CuCl}_4^-$	$\begin{array}{c} \cdot\cdot \\ :\text{Cl}: \\ \cdot\cdot \\ :\text{Cl}:\text{Cu}:\text{Cl}: \\ \cdot\cdot \\ :\text{Cl}: \\ \cdot\cdot \end{array}$
$\begin{array}{c} \text{H} \\ \cdot\cdot \\ :\text{N}:\text{H} \\ \cdot\cdot \\ \text{H} \end{array}$ Ammonia	$\text{Ag}(\text{NH}_3)_2^+$	$\begin{array}{c} \text{H} \quad \text{H} \\ \cdot\cdot \quad \cdot\cdot \\ \text{H}:\text{N}:\text{Ag}:\text{N}:\text{H}^+ \\ \cdot\cdot \quad \cdot\cdot \\ \text{H} \quad \text{H} \end{array}$
$:\text{C}\equiv\text{N}:^-$ Cyanide ion	$\text{Fe}(\text{CN})_6^-$	
$:\text{C}\equiv\text{O}:$ Carbon monoxide	$\text{Ni}(\text{CO})_4$	$\begin{array}{c} \cdot\cdot \\ \text{O} \\ \parallel \\ \text{C} \\ \cdot\cdot \\ :\text{O}=\text{C}:\text{Ni}:\text{C}=\text{O}: \\ \cdot\cdot \\ \text{C} \\ \parallel \\ \text{O} \\ \cdot\cdot \end{array}$
$\begin{array}{c} \cdot\cdot \\ :\text{O}:\text{H}^- \\ \cdot\cdot \end{array}$ Hydroxide ion	$\text{Zn}(\text{OH})_4^-$	$\begin{array}{c} \text{H} \\   \\ \text{O}^- \\ \cdot\cdot \\ \text{H}-\text{O}:\text{Zn}:\text{O}-\text{H} \\ \cdot\cdot \\ \text{O} \\   \\ \text{H} \end{array}$
$\begin{array}{c} \cdot\cdot \\ :\text{O}:\text{H} \\ \cdot\cdot \\ \text{H} \end{array}$ Water	$\text{Cu}(\text{H}_2\text{O})_4^{++}$	

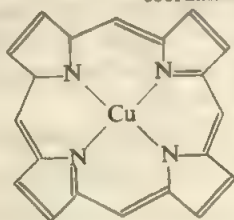
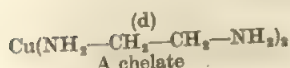
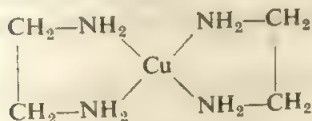
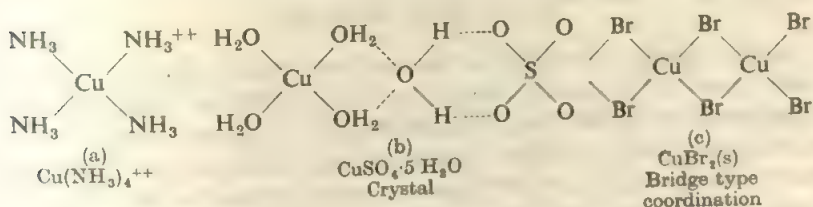
complexes listed in this chapter the coordination number is 2. Consider  $\text{Ag}(\text{S}_2\text{O}_3)_2^-$ :



(All the electrons around the oxygen and sulfur atoms are not shown).

Two pairs of electrons are contributed to and shared by silver ion. All the cupric ion and the nickelous ion complexes appearing in this discussion contain 4 groups. The cupric ion and the nickelous ion have a coordination number of +4. Both ferric and ferrous ions have a coordination number of 6 in the cyanides. The coordination number is generally the same for most complexes of a particular ion, but there are usually exceptions, such as the  $\text{Ni}(\text{H}_2\text{O})_6^{++}$ . There is little to aid one in determining the coordination number that a specific metal ion might exhibit. Those metals in the first row of 8 in the Periodic Table have coordination numbers no greater than 4, because no more than 4 groups can fit around the small ion. Metals in the second period of 8 and the first long period are limited in size to 6 surrounding groups, although some prefer only 4. Beyond that there are no limitations. One more generalization is useful. The coordination number tends to increase with an increasing positive charge on the metal ion.

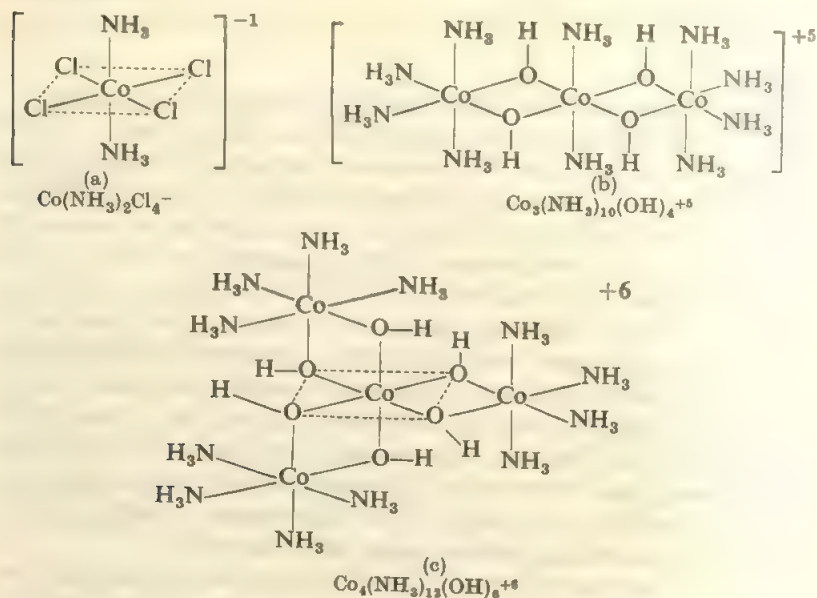
At times the empirical formulas of certain complex ions or complex compounds indicate a change in coordination number that is not real. For example, consider these series of compounds and ions.



(e)  
A porphyrin

In all these compounds the coordination number of copper is 4. Anhydrous cupric bromide is said to have a bridge type coordination that connects the

cupric ions in long chains. The copper porphyrin is related to the iron compound in hemoglobin.  $\text{Cu}(\text{NH}_2\text{-CH}_2\text{-CH}_2\text{NH}_2)_2$  is known as a chelate, a compound in which coordination occurs at two points with the same coordinating group.

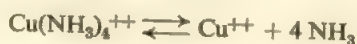


The coordination number of the cobalt ion is six in all three compounds.

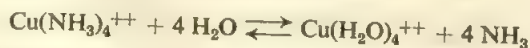
#### D. WATER OF HYDRATION

Many "simple" metal ions in solutions are actually complex ions. The water molecule was listed among complexing groups in Table 26.2. The structure of the hydrated cupric ion ( $\text{Cu}(\text{H}_2\text{O})_4^{++}$ ) appeared there as well as in the structure of crystalline copper sulfate, ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ). These ions:  $\text{Fe}^{+++}$ ,  $\text{Al}^{+++}$ ,  $\text{Ag}^+$ ,  $\text{Cu}^{++}$ ,  $\text{Ni}^{++}$  and others are hydrated in solution and in many of their crystalline compounds and should be written:  $\text{Fe}(\text{H}_2\text{O})_6^{+++}$ ,  $\text{Al}(\text{H}_2\text{O})_6^{+++}$ ,  $\text{Ag}(\text{H}_2\text{O})_2^+$ ,  $\text{Cu}(\text{H}_2\text{O})_4^{++}$  and  $\text{Ni}(\text{H}_2\text{O})_6^{++}$ . Just as the proton does not exist in solution but is hydrated to form the hydronium ion, so are these metal ions.

The equilibrium decomposition reaction of the cupric ammonia complex ion appears in Chapter 23 as:



but it might be written more properly as:



Equilibrium exists because both ammonia molecules and water molecules are competing for the cupric ion. For simplicity the ion is not usually shown

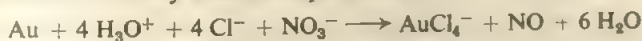


hydrated. Nevertheless, the ion is hydrated. The value of the instability constant is not altered by neglecting the water of hydration in the equation, because the solvent concentration is dropped from the expression for a dilute solution.

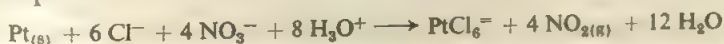
#### D. STABILITY OF METAL-CENTERED COMPLEX IONS

The stability of these complex ions varies greatly.  $\text{Mg}(\text{NH}_3)_6^{++}$  is so unstable that its existence may be determined only by a careful study of the vapor pressure of ammonia in solutions containing magnesium salts. In contrast, the cyanide ion cannot be detected even by the most precise analytical methods in solutions of either potassium ferricyanide or potassium ferrocyanide. The instability constants for these complex ions are extremely small,  $1 \times 10^{-42}$  and  $1 \times 10^{-35}$  respectively.

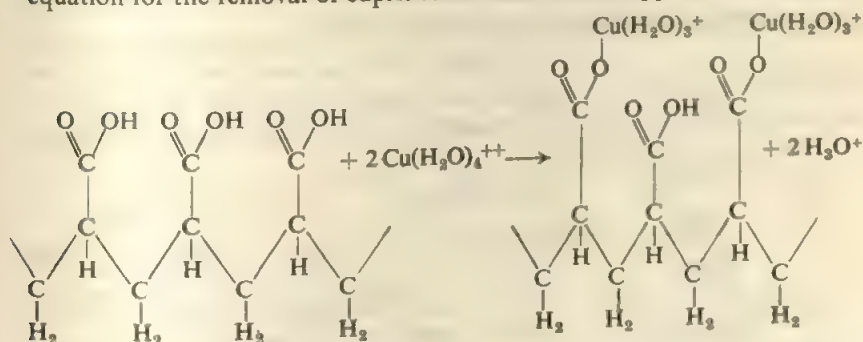
Gold dissolves in neither concentrated nitric acid nor concentrated hydrochloric acid. However, it does dissolve in a mixture of the two acids (aqua regia), not because the mixture is more acidic, but because of oxidation and formation of a very stable complex ion:



Even platinum dissolves in aqua regia, again by the formation of a very stable complex ion:

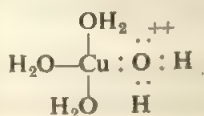


The resin in a synthetic ionic exchanger used to purify water removes metal ions because of their tendency to form a stable complex ion. A schematic equation for the removal of cupric ions from solution appears below.

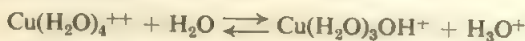


#### E. HYDROLYSIS OF METAL IONS AND AMPHOTERISM

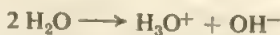
Solutions of metal ions are slightly acidic. That is, in such solutions more protons are complexed with water to form hydronium ions than is the case in water alone. The cupric ion is hydrated  $\text{Cu}(\text{H}_2\text{O})_4^{++}$ . Consider one branch of the complex ion:



Electrons are attracted by the doubly charged cupric ion. Even the pair shared between the oxygen and hydrogen is pulled toward oxygen, making the attached water molecule more polar and leaving a smaller share of the electrons for hydrogen. This reaction occurs:

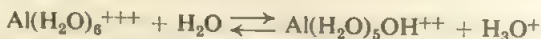


to only a small extent but to a greater extent than the ionization of water.

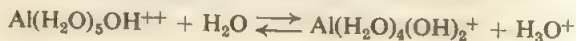


The pH of the solution is less than 7.

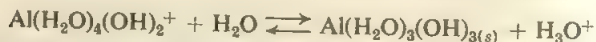
Aluminum ion is more acidic than cupric ion by the same type equilibrium reaction:



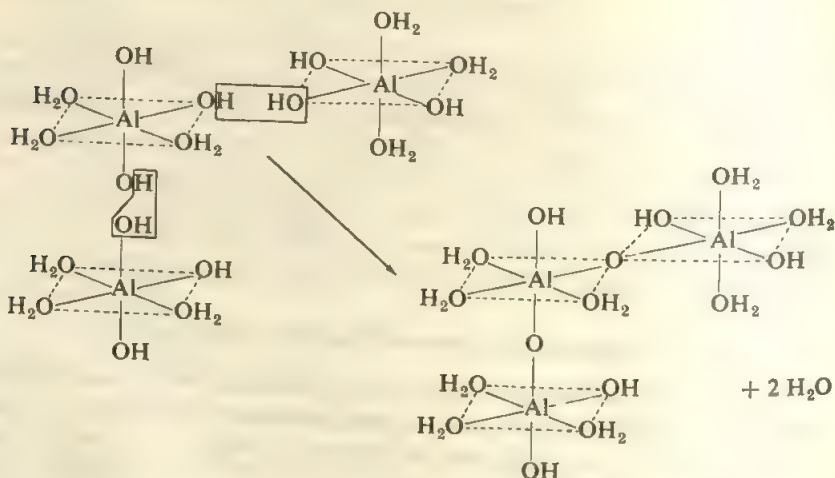
In a very dilute solution where the hydronium ion concentration remains almost  $10^{-7}$ , the reaction may proceed two steps farther:



and



As shown in the equations, when three protons are lost from a hydrated aluminum ion, a molecule (a neutral group of atoms) is formed. Not being charged, the molecule has little attraction for solvent dipoles and precipitates. The precipitate is often called hydrous aluminum oxide and is written  $\text{Al}(\text{OH})_3$ . The more correct formula is  $\text{Al}(\text{H}_2\text{O})_3(\text{OH})_3$ . But even this formula is not entirely correct, because as soon as the molecules are formed, they proceed to join together, with a loss of water:

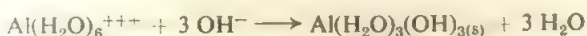


A great network of molecules soon exists as a filmy white precipitate, with the formula of  $\text{Al}(\text{H}_2\text{O})_3(\text{OH})_x\text{O}_y$ , where  $x + 1/2y = 3$ .

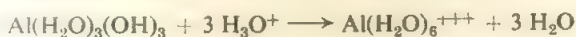
Aluminum sulfate is used at times to purify slimy water. In the dilute solution obtained by adding a few crystals to a pool of water, the hydrated

aluminum ion hydrolyzes to the hydrous aluminum oxide. The netlike precipitate settles slowly to the bottom, taking dust particles, bacteria and even color from the water.

The aluminum ion is sufficiently acidic to be titrated with a solution of a strong base such as sodium hydroxide. The addition of three times as much base (in mole quantities) precipitates the aluminum as the hydrous hydroxide:



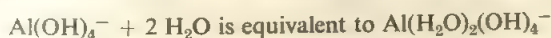
Aluminum hydroxide is a base; it dissolves in an acidic solution to reverse the three step equation above:



The hydrous hydroxide is also an acid. Hydroxide ions may take protons from the remaining tightly held water molecules, effectively exchanging them for hydroxide groups. The first step in the reaction occurs when more base is added. It is represented by this equation:



The aluminate ion ( $\text{Al}(\text{H}_2\text{O})_2(\text{OH})_4^-$ ) is commonly written as  $\text{Al}(\text{OH})_4^-$ , or as  $\text{AlO}_2^-$ . This is consistent with the practice of ignoring water of hydration or even "combined" water. "Bookkeeping" shows that

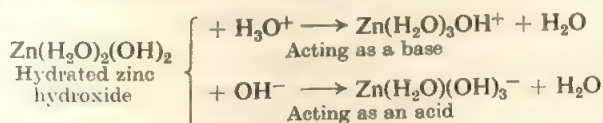


and



The simpler formulas are often used in preference to the more correct but more cumbersome notation used in this section.

Because it is both an acid and a base, aluminum hydroxide is said to be amphoteric. Zinc hydroxide is amphoteric, as shown by these equations:



Other amphoteric hydroxides (written without waters of hydration) are:  $\text{Be}(\text{OH})_2$ ,  $\text{Cr}(\text{OH})_3$ ,  $\text{Zn}(\text{OH})_2$ ,  $\text{Sn}(\text{OH})_4$ ,  $\text{Pb}(\text{OH})_2$ ,  $\text{As}(\text{OH})_3$  and  $\text{Sb}(\text{OH})_3$ . Notice that the metals in the formulas fall near the diagonal line separating metals and non-metals in the Periodic Table. They are among the most electronegative of the metals, and therefore hold complexing groups through the shared pair of electrons, most tightly. The hydroxide and water groups are held so securely that aluminum hydroxide and zinc hydroxide are covalent and not ionic compounds. This makes the acidic behavior possible. Protons could not be pulled away unless the water molecules in the hydroxide were held tightly.

Hydroxides of active metals (electropositive metals), such as barium hydroxide,  $\text{Ba}(\text{OH})_2$ , are basic but not acidic.  $\text{Ba}(\text{H}_2\text{O})_x\text{OH}^+$  does not exist as a

Table 26.3 Colors of

<u>Na</u>	<u>Mg</u>			
NaCl colorless	MgBr <sub>2</sub> colorless			
NaClO colorless	MgSO <sub>4</sub> colorless			
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10 H <sub>2</sub> O colorless	MgC <sub>2</sub> O <sub>4</sub> ·2 H <sub>2</sub> O colorless			
Na <sub>2</sub> CO <sub>3</sub> ·10 H <sub>2</sub> O colorless	MgNH <sub>4</sub> PO <sub>4</sub> ·6 H <sub>2</sub> O colorless			
<u>K</u>	<u>Ca</u>	<u>Sc</u>	<u>V</u>	<u>Mn</u>
KOH colorless	CaS colorless	Sc <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ·5 H <sub>2</sub> O colorless	VSO <sub>4</sub> ·7 H <sub>2</sub> O violet	KMn(SO <sub>4</sub> ) <sub>2</sub> ·12 H <sub>2</sub> O violet
KClO <sub>4</sub> colorless	Ca <sub>3</sub> N <sub>2</sub> lt. brown	Sc <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·6 H <sub>2</sub> O colorless	(VO) <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> red	KMnO <sub>4</sub> dk. purple
K <sub>2</sub> SO <sub>3</sub> ·2 H <sub>2</sub> O colorless	CaCl <sub>2</sub> ·6 H <sub>2</sub> O colorless	ScCl <sub>3</sub> colorless	VOCl yel. brown	MnCl <sub>2</sub> pink
K <sub>2</sub> Al <sub>2</sub> O <sub>4</sub> ·3 H <sub>2</sub> O colorless	Ca(ClO) <sub>2</sub> ·4 H <sub>2</sub> O colorless	Sc(NO <sub>3</sub> ) <sub>3</sub> colorless	VF <sub>3</sub> br. yel.	MnCl <sub>2</sub> ·4 H <sub>2</sub> O red
				MnCl <sub>4</sub> red-brown
		<u>Ti</u>		<u>Cr</u>
		TiS reddish		Cr <sub>2</sub> O <sub>3</sub> green
		TiCl <sub>3</sub> dk. violet		CrCl <sub>3</sub> ·10 H <sub>2</sub> O green
		Ti <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> green		Cr(PO <sub>4</sub> ) <sub>2</sub> ·2 H <sub>2</sub> O violet
		Ti <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ·10 H <sub>2</sub> O yellow		PbCrO <sub>4</sub> yellow
				K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> orange
	<u>Ce</u>	<u>Pr</u>		<u>Nd</u>
	CeCl <sub>3</sub> colorless	PrBr <sub>3</sub> green		NdCl <sub>3</sub> rose-violet
Rare Earths	Ce(BrO <sub>3</sub> ) <sub>3</sub> ·9 H <sub>2</sub> O reddish-white	PrCl <sub>3</sub> ·7 H <sub>2</sub> O green		Nd <sub>2</sub> S <sub>3</sub> olive green
	Ce(SO <sub>4</sub> ) <sub>2</sub> ·4 H <sub>2</sub> O yellow	Pr <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ·10 H <sub>2</sub> O lt. green		Nd <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·8 H <sub>2</sub> O red



# Certain Inorganic Compounds

			<u>Al</u>
			$\text{AlF}_3$ colorless
			$\text{AlCl}_3 \cdot 6 \text{H}_2\text{O}$ colorless
			$\text{AlI}_3 \cdot 6 \text{H}_2\text{O}$ white-yel.
			$\text{Al}_2\text{S}_3$ yellow
			$\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$ colorless
	<u>Co</u>	<u>Cu</u>	<u>Ga</u>
	$\text{CoBr}_2$ green	$\text{Cu}(\text{CN})_2$ yellow-green	$\text{Ga}_2(\text{C}_2\text{O}_4)_3 \cdot 4 \text{H}_2\text{O}$ white
	$\text{CoCO}_3$ colorless	$\text{Cu}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$ blue	$\text{GaCl}_3$ colorless
	$\text{Co}(\text{IO}_3)_2 \cdot 6 \text{H}_2\text{O}$ blue	$\text{Cu}_2\text{C}_2$ red	$\text{Ga}_2\text{O}$ br. black
	$\text{Co}(\text{CN})_2 \cdot 2 \text{H}_2\text{O}$ bluish-violet	$\text{CuCl}_2$ yellow	
	$\text{K}_3\text{Co}(\text{CN})_6$ yellow	$\text{Cu}_2\text{S}$ black	
<u>Fe</u>		<u>Ni</u>	<u>Zn</u>
$\text{FeBr}_3$ red-brown		$\text{Ni}_2\text{S}_3$ yellow	$\text{ZnCl}_2$ colorless
$\text{K}_3\text{Fe}(\text{CN})_6$ red		$\text{NiCO}_3$ lt. green	$\text{ZnCl}_2 \cdot 2 \text{NH}_3$ colorless
$\text{Fe}(\text{CO})_5$ dk. green		$\text{Ni}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ green	$\text{Zn}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ colorless
$\text{KFeFe}(\text{CN})_6 \cdot \text{H}_2\text{O}$ dk. blue		$\text{Ni}(\text{NO}_3)_2 \cdot 6 \text{NH}_3$ blue	$\text{Zn}(\text{BrO}_3)_2 \cdot 6 \text{H}_2\text{O}$ white
$\text{Na}_3\text{Fe}(\text{C}_2\text{O}_4)_3 \cdot 5 \text{H}_2\text{O}$ green		$\text{Ni}(\text{ClO}_3)_2 \cdot 6 \text{H}_2\text{O}$ dk. red	$\text{Zn}_3(\text{PO}_4)_2 \cdot 4 \text{H}_2\text{O}$ colorless
<u>Sm</u>	<u>Eu</u>		
$\text{SmI}_2$ or. yellow	$\text{EuCl}_3$ yellow		
$\text{SmCl}_3$ red-brown	$\text{Eu}_2\text{O}_3$ pale rose		
$\text{Sm}(\text{NO}_3)_3 \cdot 6 \text{H}_2\text{O}$ pale yel.	$\text{Eu}_2(\text{SO}_4)_3 \cdot 8 \text{H}_2\text{O}$ pale rose		

unit in solutions. The large barium ion surrounded by an indefinite and changing number of water molecules remains free of the hydroxide ions present in solution. The hydrous precipitate,  $\text{Ba}(\text{OH})_2 \cdot 8 \text{H}_2\text{O}$ , is best represented by the formula,  $\text{Ba}(\text{H}_2\text{O})_8 \cdot 2 \text{OH}^-$ . Water molecules about the large barium ion are not held sufficiently secure that a proton might be pulled away. Transition metal hydroxides tend to be co-valent and show slight amphoteric properties, but the effect becomes significant only for the hydroxides of metals having sufficient electronegativity to form very stable complexes with oxygen.

### F. COLOR IN INORGANIC COMPOUNDS AND IONS

Almost all colored inorganic substances contain metals from the central portion of the Periodic Table. Conversely, practically no substances containing only metals from Groups IA, IIA and IIIA of the table are colored. In Table 26.3 color is found among compounds containing either rare earth or transition elements.

A substance is colored only when it absorbs part of the light in the visible spectrum. If a substance absorbs light of a wavelength corresponding to blue light, and reflects the balance of the spectrum it will appear red, orange or yellow. The color of a substance is complementary to the color absorbed.

Certain structural features of molecules or ions are either necessary or helpful in absorbing the low energy photons of visible light: (1) Energy levels within the substances must be closely spaced. The energy change of the excited electron must be exactly equal to the relatively low energy of the absorbed photon. (2) The substances should contain unpaired electrons. Paired electrons are stable as a unit. Too much energy is required to separate one from another and lift it to a higher level. (3) Covalent bonding favors the appearance of color.

The unfilled sub-group in the electron levels of transition metal ions are close together. Little energy difference exists between the orbits for the electrons 9 to 18 in the metal *ion's* outermost level. Unpaired electrons can appear in these metal ions, because some have an odd number of electrons, whereas nontransition metals have 8 (4 pair). Furthermore, the electrons in the uncompleted shell of the transition elements tend not to pair but to fill one in each orbit until all are occupied. Thus, an ion might contain an equal number of electrons and yet contain unpaired electrons. When coordination occurs, to form either a complex ion or covalent bonds within a compound, the incoming electrons may fill all the available closely spaced levels or may force the electrons to pair. However, this may not be the case and a colored compound or ion results.

Not enough is known of the relationship of color to ion or compound structure. However, one might expect that changing the complexing groups would change the spacing of the energy levels in an atom slightly, thus changing the color. This effect may be observed.  $\text{NiBr}_2$  is yellow;  $\text{Ni}(\text{SCN})_2$  is brown; and  $\text{NiI}_2$  is black. Solutions of the nickel complex ions have these colors:  $\text{Ni}(\text{NH}_3)_4^{++}$ , blue;  $\text{Ni}(\text{CN})_4^-$ , buff; and  $\text{Ni}(\text{H}_2\text{O})_4^{++}$ , green.

## EXERCISES

1. Define and give an example of each:
  - a. metal (chemical sense)
  - b. active metal
  - c. common metal
  - d. transition element
  - e. complex ion
  - f. metal-centered complex ion
  - g. coordinate bond
  - h. amphoteric hydroxide
  - i. acidic solution
2. Why do transition elements exhibit two different ionic valences while the active metals do not?
3. Describe the steps in black and white photography starting with an unexposed film.
4. What is the common coordination number of:
  - (a) silver ion, (b) cupric ion, (c) ferric ion, (d) aluminum ion, (e) cobalt ion?
5. Write the formulas of a complex ion for each of the metal ions listed in Question 4.
6. What kind of bonds are usually found in complex ions?
7. Explain what happens when blueprint paper is exposed. When it is developed.
8. What characteristics of metal ion and complexing group favor formation of complex ions?
9. What is the coordination number of a metal ion?
10. Which formula for aluminum hydroxide is most correct from a structural standpoint:  $\text{Al}(\text{OH})_3$ ,  $\text{Al}(\text{OH})_3 \cdot 3 \text{H}_2\text{O}$ , or  $\text{Al}(\text{H}_2\text{O})_3(\text{OH})_3$ ? Is any one of these completely satisfactory? Explain.
11. Account for the fact that gold dissolves in a mixture of concentrated nitric and hydrochloric acids but it dissolves in neither separately.
12. Which holds hydrate molecules more tightly, the aluminum ion or the sodium ion? Which metal is more electronegative?
13. Explain why aluminum hydroxide might be both an acid and a base, whereas calcium hydroxide is a base only and sulfur oxy hydroxide,  $\text{HOSO}_3\text{OH}$ , is an acid only.
14. What three characteristics is a colored ion likely to have?
15. Which of the following are colored?
  - a.  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$
  - b.  $\text{Al}(\text{H}_2\text{O})_3(\text{OH})_3$
  - c.  $\text{AgCl}$
  - d.  $\text{CrO}_4^{=}$
  - e.  $\text{KCl}$
  - f.  $\text{Fe}(\text{CN})_6^{=}$
  - g.  $\text{Ba}(\text{OH})_2 \cdot 8 \text{H}_2\text{O}$

## THE NUCLEUS AND CHEMISTRY

### 1. INTRODUCTION

A large volume of literature has accumulated from the many scientific investigations of the nuclei of atoms. Much is, therefore, known about these nuclei, the tiny though massive centers of atoms. The composition of nuclei are expressed in terms of the kinds and numbers of nucleons (protons and neutrons) they possess. In every case, except for the lightest isotope of hydrogen, all nuclei are composed of protons and neutrons. Nuclei having certain numbers of neutrons appear to be more prevalent. Structurally, it appears that there are energy levels for nucleons in the nucleus as there are for extranuclear electrons about the atom. Within nuclear energy levels there are also sublevels which, when they are filled with nucleons, lend a stability to the nucleus not unlike the stability of the "filled octet" in the electron structure of atoms and ions. Theories have been developed to explain the nature of the forces necessary to hold comparatively massive particles (protons) bearing the same charge in such a tiny nuclear volume. Studies of these fascinating topics, however, must be left for classes in nuclear physics. This chapter will be devoted to other, equally fascinating aspects of the subject: gross nuclear changes, the change in chemical identity associated with the nuclear reactions, the energies involved and the usage made of nuclear changes and of the products of those changes. The discussion will be divided into five parts: (a) a discussion of nuclear composition as it relates to the size of atoms and their position in the Periodic Table (some facts presented in Chapter 6, Atomic Structure, will be repeated here), (b) mass and energy relationships, (c) the decay (radioactive decay) of larger nuclei (with the formation of new atoms), (d) nuclear fission and (e) atomic fusion (union of smaller nuclei). Applications will be interwoven into the discussion.



## 2. COMMON FACTS ABOUT NUCLEI

The nucleus may be assumed to be composed of neutrons and protons only. Other sub-atomic particles have been discovered, about 30 in number (mesons,  $V$  particles, etc.). Some may well exist in the nucleus, but, if so, they are there at the expense of the nucleons. The remaining type of particle found in the atom is the electron. The electrons occupy the volume about the nucleus.

The composition of the nucleus of an atom is shown by a sub number and a super number preceding the symbol.  $^{16}_8\text{O}$  represents the common oxygen atom. It contains 16 nucleons, 8 of which are protons and 8 neutrons.  $^{238}_{92}\text{U}$  is the uranium atom containing 92 protons and a total of 238 nucleons, or  $238 - 92 = 146$  neutrons. 238, the nucleon total, is called the mass number.

Atoms are numbered and named according to the number of protons in the nucleus. The proton number is the so-called atomic number. All atoms of the same element have the same atomic number. Atoms are arranged in the Periodic Table in order of increasing atomic number. Most elements contain isotopes. Isotopes are atoms of the same name with different masses, and are, therefore, atoms having the same number of protons but possessing a different number of neutrons. Usually, stable isotopes of the same element differ by only one or two neutrons. For tin, an exception, 10 naturally occurring isotopes have been found.

Among the lighter naturally occurring atoms the number of protons and neutrons is about equal. However, as the number of protons increases, the ratio (number of neutrons to number of protons) increases. Figure 27.1 is a plot of the number of neutrons versus the number of protons for a typical group of atoms. Apparently this increasing number of neutrons above

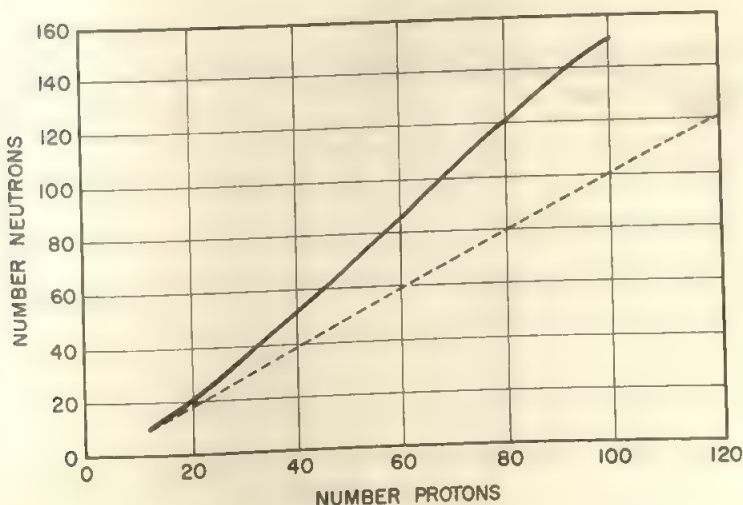


Figure 27.1. Plot of neutrons/protons for typical nuclei.

protons is necessary for the stability of the larger nuclei. In the heavier nuclei the ratio, neutrons to protons, slightly exceeds 1.5 to 1.

### 3. NUCLEAR MASS AND ENERGY

Of great import is the fact that the mass of the nucleus of an atom is not equal to but less than the combined masses of its separate nucleons. For example, the nucleus of the common isotope of carbon,  $^{12}_6\text{C}$ , has a mass of 12.0038 atomic mass units (amu), the scale used by the physicist. It contains 6 protons, each with a mass of 1.00814 amu and 6 neutrons, each of which separately has a mass of 1.00897.

Mass defect =  $\frac{\text{sum of individual masses of nucleons present} - \text{observed mass}}{\text{mass}}$

Mass defect =  $6 \times 1.00814 + 6 \times 1.00897 - 12.0038 = 0.0989$  amu

Obviously, mass would not be conserved were 6 neutrons and 6 protons to combine to form a  $^{12}_6\text{C}$  nucleus. Instead, some mass, 0.0989 amu, would disappear. It is converted to energy. Using Einstein's equation for mass energy equivalence,  $E = mc^2$ , one finds that  $2.14 \times 10^{12}$  calories of heat would be liberated were the necessary neutrons and protons brought together to form 1 mole of carbon-12 nuclei. This is equivalent to the energy from  $6 \times 10^5$  lbs of coal. Dividing the mass defect by 12 and expressing the value in terms of an energy unit, mev (million electron volts), one arrives at a quantity called the binding energy per nucleon. This is, in fact, the binding energy, since it is the energy which must be invested for each of the twelve nucleons of carbon-12 to separate the atom into its particles.

The binding energy curve for the atoms appears in Figure 27.2. The binding energy per nucleon for each atom is plotted versus the mass number (the number of nucleons). One can see that atoms of a total mass of approxi-

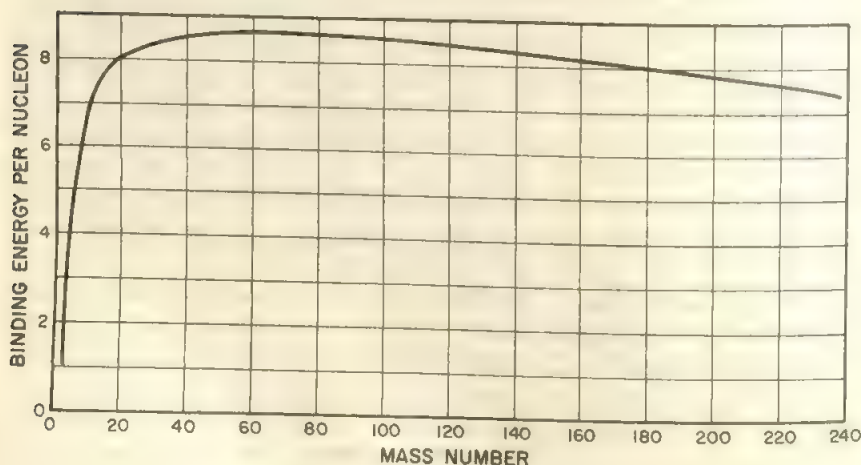


Figure 27.2. Binding energy.

mately 60 have the greatest binding energy per nucleon. The binding energies per nucleon gradually decrease for atoms with a mass number greater than 60 and decrease steeply from this maximum for atoms of smaller mass number. Obviously, if larger nuclei are separated into smaller fragments (about mass number 60) energy must be released, and if tiny nuclei are combined into larger nuclei still greater energies must be liberated.

#### 4. RADIOACTIVE DECAY

##### A. THE DECAY PROCESS

Larger nuclei (those with a greater number of protons) are less stable than smaller nuclei. This can be seen in the fact that smaller atoms are much more abundant as shown in the analysis of the earth's crust. Table 27.1 shows the percentages of the most abundant elements.

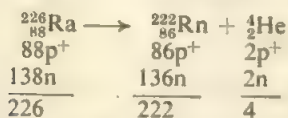
Futhermore, all atoms with an atomic number greater than 83 are radioactive. That is, they undergo a spontaneous loss of alpha particles, beta particles or gamma radiation, or all three. The nature of some types of radiation was studied in Chapter 6, where it was noted that alpha rays bend very gradually toward the negative of an electric field, that beta particles bend sharply toward the positive, and that gamma rays follow a straight path through a transverse electric field. Quantitative tests of the degree of bending show the alpha ray to be a particle, a helium nucleus ( $\text{He}^{++}$ ) in motion, and

**Table 27.1. Percentage of Elements in Earth's Crust  
(A. E. Fersman [1939])**

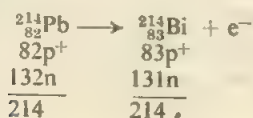
Oxygen	49.13
Silicon	27.72
Aluminum	8.13
Iron	5.0
Calcium	3.63
Sodium	2.83
Potassium	2.59
Magnesium	2.09
Titanium	0.44
Hydrogen	0.15
Phosphorus	0.12
Carbon	0.03
Chlorine	0.03
Strontium	0.03
Nitrogen	0.005
Cobalt	0.002
Platinum	$2 \times 10^{-5}$
Gold	$5 \times 10^{-7}$

the beta particle to be an electron. The gamma ray is a high-energy light ray similar to an X-ray.

The spontaneous loss of tiny particles from the nucleus is known as radioactive decay, for in losing the particles (or radiation) the atom decreases in mass and changes from one atom into another in sequence, until, with radium, a stable lead atom results. One can follow the pathway of the changes and note the kind of atom found as each ray is lost. The first step in the decay of radium is the loss of an alpha particle:



Because the alpha particle (a helium nucleus) contains 2 protons and 2 neutrons, the new atom formed has a mass 4 units less than the parent atom and an atomic (proton) number decreased by 2; hence is radon of atomic number 86 and mass 222. Whereas the loss of an alpha particle decreases the atomic number by 2, the loss of a beta particle (an electron from the nucleus) increases it by 1. An unusually massive isotope of lead,  ${}^{214}_{82}\text{Pb}$ , loses a beta particle:



In effect, in the nucleus, a neutron is converted to a proton, (assumes a +1 charge) with the loss of an electron. Gamma radiation, on the other hand, merely reduces the internal energy of an atom but does not change its identity.

The radium decay series, which shows the atoms obtained after each radiation or particle loss, is shown in diagram form in Table 27.2. An increase in atomic number is shown by a move to the right and a decrease by a move to the left.

Uranium, protactinium and thorium, elements 92, 91 and 90, the largest naturally occurring atoms, are all radioactive and decay by loss of beta particles and alpha particles in a stepwise fashion through radium to lead.

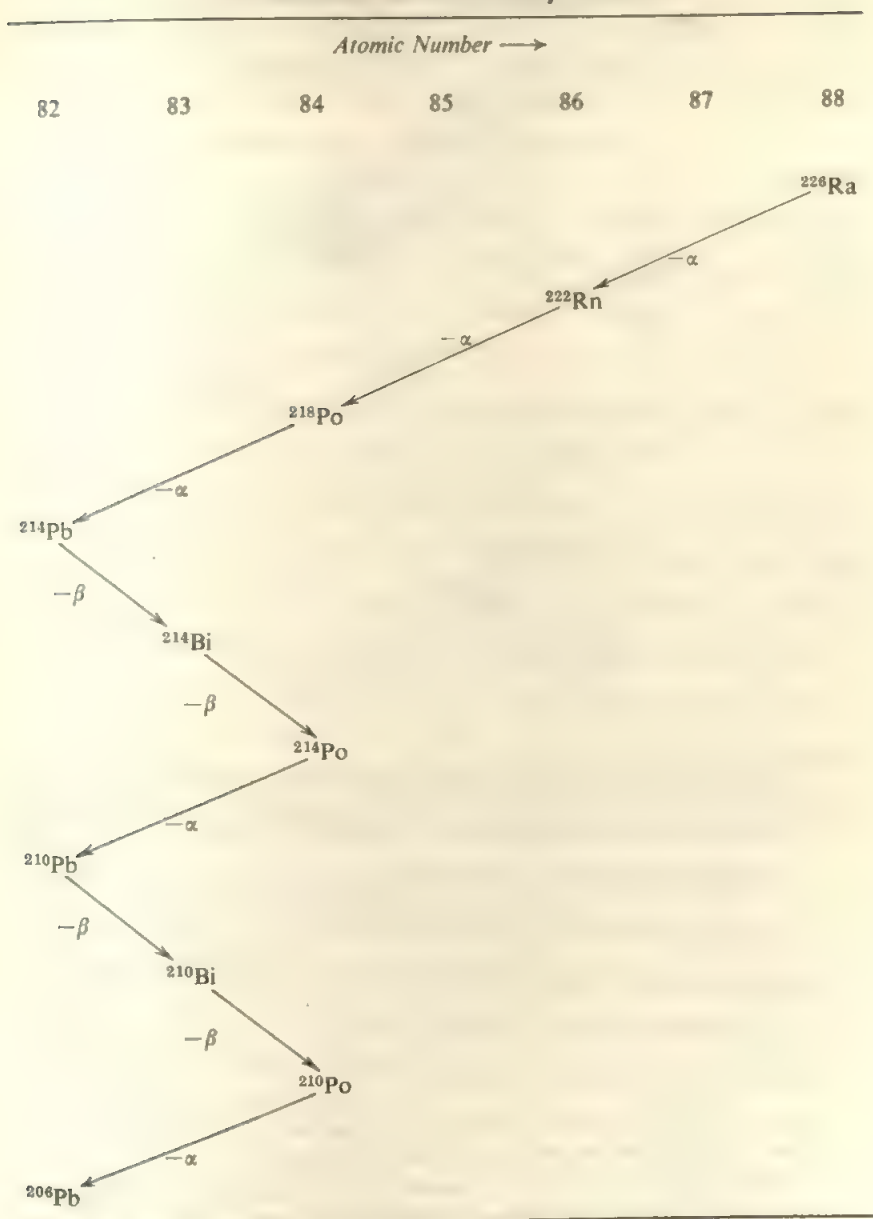
## B. DETECTION OF RADIOACTIVE DECAY

There are a variety of methods to detect radioactive decay.

1. Gamma radiation exposes *photographic film*. This exposure may be accomplished even through the wrapping.
2. Paint, which fluoresces when bombarded with alpha particles, when mixed with a small amount of radium glows at night on watch faces.
3. When gamma rays pass through a gas at low pressure between charged electrodes, it ionizes the gas. The ions formed are drawn to the charged electrodes causing a sudden surge of current, which causes the flick of a



Table 27.2. Radium Decay Series



galvanometer needle, or a click in a counter. The tube containing the charged electrodes is called a Geiger tube and is the essential feature of the instrument called a Geiger counter (Fig. 27.3).

Connected to a counter, a Geiger tube will measure radiation intensity. Geiger counters, a Geiger tube plus a device for counting the surges of

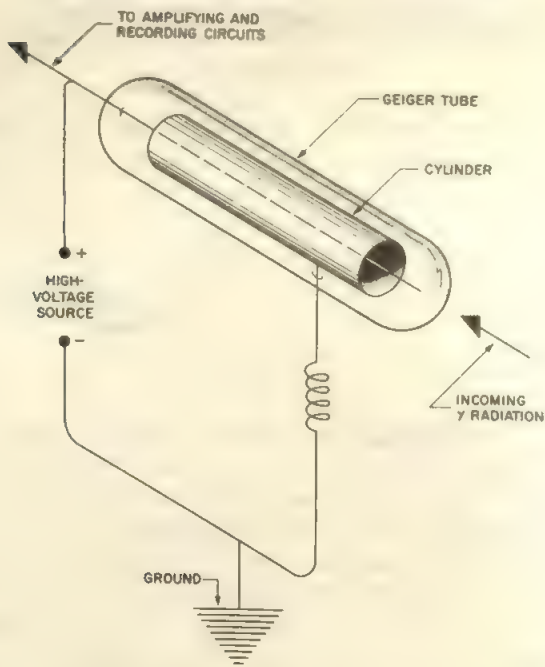


Figure 27.3. A  $\gamma$  ray on a Geiger tube.

electricity, are carried over the desert in searches for deposits of radioactive uranium and are widely used for monitoring natural radiation.

Radioactive material and a Geiger counter can be used to carry out very interesting studies. For example, one can add a radioactive solute to a body of water, then by monitoring springs below with a Geiger counter, can determine which are fed by the reservoir above. One can determine the volume of blood in the body by admitting a small measured sample of blood containing radioactive material with a known radiation count. After the blood is completely mixed, a like sample of blood will exhibit a count reduced by the dilution factor. One can follow a radioactive chemical from a nutrient solution up the roots and stem of a plant to see where that chemical accumulates. Radioactive iodine is used to determine the activity of the thyroid gland.

4. Possibly the most accurate measure of the quantity of radiation is through a direct analysis of radiating material. Alpha and beta radiation changes the identity of the atoms.
  - (a) An alpha-emitting sample may be enclosed in a gastight evacuated container. Helium gas accumulates, one atom per each alpha particle. The pressure of the helium is a measure of the amount of radiation.
  - (b) One can perform a mass analysis. If the radiating sample is a gas or can be vaporized it can be admitted to an ionization chamber of

a mass spectrograph where fragments of molecules, parent atoms and products are separated because of a mass difference.

- (c) Chemical analysis reveals the amount of accumulated radiation products and is a measure of the radiation time and intensity.

### C. RATES OF RADIOACTIVE DECAY

Radioactive decay is a first-order process, that is, it changes at a rate which depends only upon the concentration or amount of decaying material present. A certain fraction of the unstable atoms present, regardless of the total number, decays in a certain period of time. The rates of radioactive decay reactions are compared by half-lives. The half-life is the time required for one half of the atoms to decay. This time is the same for the same material regardless of the mass of the sample.

Different radioactive species have different half-lives and, therefore, decay at different rates. The half-life may vary from a micro-second to a thousand years. Some typical half-lives are shown in Table 27.3.

No conditions of pressure or temperature short of the temperatures existent on the stars or in the center of an atomic explosion have been found to alter the rate of radioactive decay. This principle is used when using radioactivity to determine the age of the earth. If one assumes that deposits of radioactive material were pure parent material at the creation of the earth (and the universe), from the half-life of the process and the relative amounts of parent and daughter material present one can calculate the age of the earth. Estimates of the earth's age by this method are about 5.5 billion years.

Age determination by carbon dating assumes that while the tree lived, from which a manuscript or an object was made, it contained the normal percentage of radioactive carbon,  $^{14}_6\text{C}$ , in its fibers. When the tree died, no

**Table 27.3. Half-lives for Certain Decay Reactions**

<i>Reaction</i>		<i>Half-life</i>
$^3_1\text{H}$	$\longrightarrow$ $^3_2\text{He} + \beta^-$	12.4 years
$^{14}_6\text{C}$	$\longrightarrow$ $^{14}_7\text{N} + \beta^-$	5568 years
$^{32}_{15}\text{P}$	$\longrightarrow$ $^{32}_{16}\text{S} + \beta^-$	14.3 days
$^{35}_{16}\text{S}$	$\longrightarrow$ $^{35}_{17}\text{Cl} + \beta^-$	87.1 days
$^{131}_{53}\text{I}$	$\longrightarrow$ $^{131}_{54}\text{Xe} + \beta^-$	8.07 days
$^{90}_{38}\text{Sr}$	$\longrightarrow$ $^{90}_{39}\text{Y} + \beta^-$	27.7 years
$^{221}_{88}\text{Ra}$	$\longrightarrow$ $^{217}_{86}\text{Rn} + \alpha$	30 seconds
$^{234}_{92}\text{U}$	$\longrightarrow$ $^{230}_{90}\text{Th} + \alpha$	$2.48 \times 10^5$ years
$^{257(?)_{103}}\text{Lw}$	$\longrightarrow$ $^{253}_{101}\text{Md} + \alpha$	8 seconds
$^{60}_{27}\text{Co}$	$\longrightarrow$ $^{56}_{25}\text{Mn} + \alpha$	5.26 years

$\alpha$  = Alpha particle

$\beta^-$  = Beta ray (electron)

more radioactive carbon could enter by respiration of carbon dioxide in the leaves. The radioactive carbon in the wood decays, and its percentage and radioactivity (count) decrease with time. The less the radioactivity (slower the count) found, the older the manuscript.

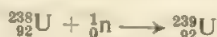
### D. ATOMIC SYNTHESIS

Larger atomic nuclei, already radioactive, will often absorb another particle hurled into them. The resultant nuclei are also usually radioactive. In 1939, Enrico Fermi proposed that atoms of atomic number greater than 92 (uranium then being the largest atom known) could be made by bombarding uranium nuclei with neutrons.

In the period of time since 1940, atoms of 11 new elements, up to and including element of atomic number 103, have been made. All have been synthesized by a similar process. Particles are hurled into the nucleus. Capture of the particle by the nucleus is followed by the radioactive emission of another or other particles.

In 1940 the common uranium isotope of mass 238 was irradiated with neutrons. The following reactions occurred:

- (a) Capture of a neutron gave uranium 239



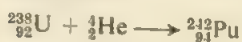
- (b)  ${}_{92}^{239}\text{U}$  then emitted a beta particle to yield an atom of a new element having atomic number 93. This element was named neptunium.



- (c) Subsequent emission of a second beta particle gave an atom of another, then new element which was named plutonium.



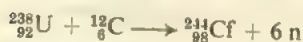
- (d) Americium was gained by capture of colliding alpha particles by uranium 238



followed by beta emission



The larger transuranic elements, those above atomic number 97 (through 103), have been prepared since 1954 by bombardment of heavy nuclei with charged nuclei of small atoms using the cyclotron. For example, californium was prepared as shown below:



## 5. NUCLEAR FISSION AND FUSION

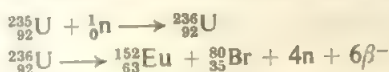
### A. NUCLEAR FISSION

A radically different type of nuclear reaction can occur when heavy atomic nuclei absorb neutrons. Absorption of slow neutrons with the eventual



elimination of a beta particle converted uranium-238 into neptunium, a new element as discussed in the preceding section. However, when the uranium-238 atom is bombarded with fast neutrons with an energy exceeding 1 million electron volts, the neutron is absorbed and fission results. The huge atom is separated into two smaller atoms.

Uranium-235, the rarer of the two isotopes of uranium (0.7% in natural deposits), suffers fission after absorbing only thermal (slow) neutrons. One cannot predict which of a variety of possible nuclear products will be obtained. One possible reaction sequence could yield:



Because the neutron to proton ratio is greater among heavier atoms, (Fig. 27.1), the two large fission products cannot be the only fission products. Either neutrons must be expelled or beta particles must be emitted (converting neutrons in the nucleus to protons). Actually, both processes occur. Gamma radiation accompanies nuclear fission but the number of rays emitted bears no direct relationship to the composition of the 2 nuclei formed. Many other pairs of nuclei are possible, each accompanied with neutrons or beta rays or both. Because neutrons are both a product of the reaction and an initiating reactant, a so-called "chain reaction" can occur. Once the reaction is initiated, neutrons from fission can be absorbed by other nuclei, sustaining the reaction (Fig. 27.4).

A glance at the binding energy curve (Fig. 27.2) shows that the two new nuclei have greater binding energy per nucleon than the large parent atom. Mass is lost and converted into energy in the division of the nucleus. The energy is released both as gamma rays and as kinetic energy in the motion of the fragments as they are hurled apart. The large release of energy per each fission and the propagation of the reaction by emitted neutrons make possible the atomic bomb. All that is necessary to achieve an explosion is to get the atoms of uranium-235 or plutonium close enough together, so that neutrons from a first chance fission are not lost but that more than one nucleus is caused to explode from the neutrons of that first event and each succeeding fission. The fuel is enriched almost to that point and then placed in the bomb. By implosion, the atom fuel is compressed beyond the critical limit and the bomb explodes.

The same principle is active in an atomic reactor. Atomic fuel is built in a "honeycomb" structure. Rods of a neutron absorber are inserted in the holes. Withdrawing the rods allows the reaction to proceed slowly. By partially withdrawing or re-inserting the rods the reaction can be controlled. Heat caused by the collision of the high velocity fission fragments is used with proper heat exchangers to form steam which drives turbines to produce electric power.

## B. NUCLEAR FUSION

At particle energies corresponding to the temperature on the sun, two very

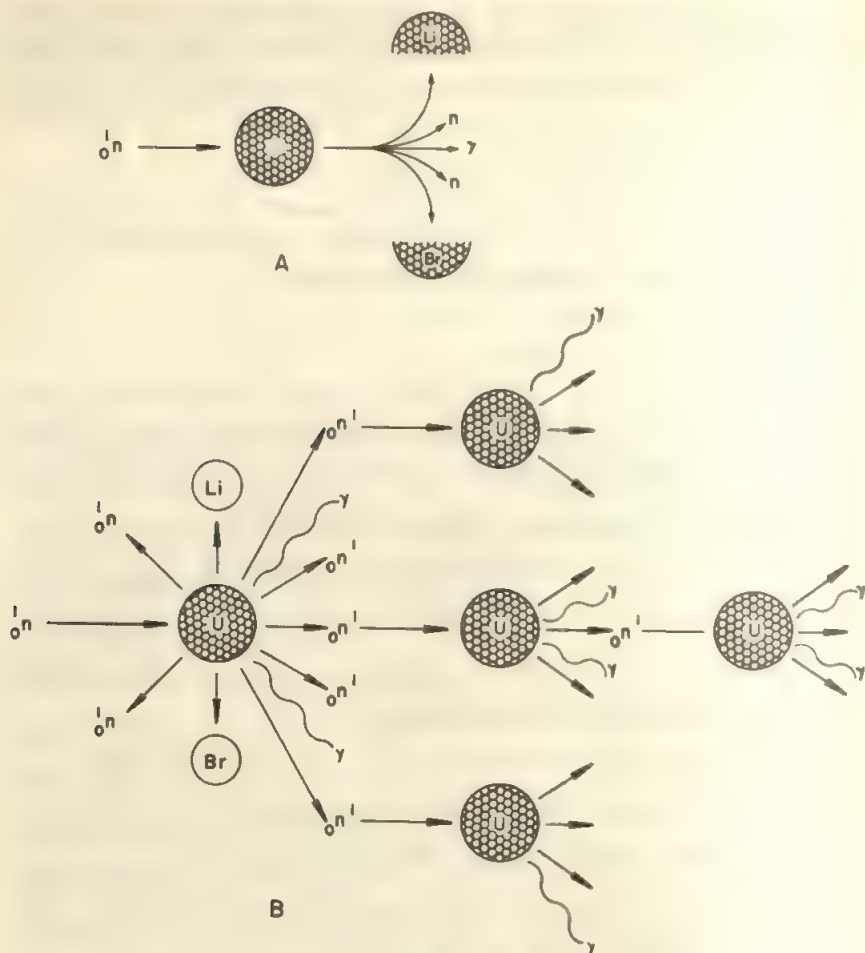
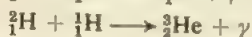
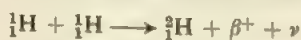


Figure 27.4. Nuclear chain fission.

small, nuclei, upon collision, may join together (fuse) to form a larger nucleus. Such reactions are thought to occur on the sun:



The result of this three-step process is the conversion of 4 hydrogen nuclei to one helium nucleus, a neutrino,  $\nu$ , a positron  $e^+$  and (according to Figure 27.2) a tremendous amount of energy. Atomic fission temperatures are sufficient to initiate reactions similar to these. In the so-called hydrogen bomb, fusion reactions are triggered by atomic fission. Reactions similar to those of the set of three shown above are called thermonuclear reactions.

## 6. BIOLOGICAL EFFECTS

*Living organisms* are damaged by the radiation resulting from radioactive decay. The radiation is capable of breaking covalent chemical bonds which can cause irreparable damage, leading to sickness and even death. Genetic damage, referred to as mutation, can result from radiation. Much is done in bacterial radiation to study these effects.

Radioactive chemicals are used to treat cancer. They are useful because of their ability to destroy tissue. Just as they can destroy normal cells, the radiation also destroys abnormal cells. One hopes for destruction of the cancerous cells with a minimum destruction of healthy tissue.

## EXERCISES

1. What justification might there be in the assumption that smaller nuclei are more stable than larger atomic nuclei, just because a very great percentage of all naturally occurring atoms has an atomic number less than 30?
2. Why should a large nucleus be less stable than a smaller nucleus?
3. Why must a smaller nucleus (with more than one proton) have approximately the same number of protons as neutrons?
4. Why should a large nucleus contain more neutrons than protons?
5. How does the absorption of an alpha particle by the nucleus change the atomic number and the mass number of an atom? Will it change the chemical properties?
6. Two identical atoms lose an identical particle, one a beta particle, the other a valence electron. How do the resulting "atoms" differ?
7. An unstable atom has a greater neutron to proton ratio than stable atoms. Describe two possible decay processes to restore a stable ratio.
8. Describe the following nuclear processes:
  - (a) fission
  - (b) fusion
  - (c) decay
  - (d) absorption
9. Why must fission of a large nucleus always be accompanied by or be followed by other radiations?
10. Why is "mass defect" coupled with "binding energy"?
11. A polonium 218 atom loses (in order) an alpha particle, a beta, a beta, an alpha, and a beta. Show in number notation such as  ${}_{84}^{218}\text{Po}$  all atoms formed in the decay series.

# CARBON AND SILICON

[illegible]

## THE GROUP IV ELEMENTS—GENERAL CHARACTERISTICS

The elements of Group IV of the Periodic Table—carbon, silicon, germanium, tin and lead—lie midway between the most active metals and the most active non-metals. Each element of Group IV has 4 valence electrons: 4 more electrons than the preceding inert gas and 4 fewer electrons than the succeeding inert gas. At first one might suppose that these elements should be the real “transition elements,” i.e., perhaps able to lose 4 electrons and become a metal or to gain 4 electrons and become a non-metal. However, when one remembers the relative electronegativity of the elements in the table and recalls that elements of like electron-attracting power lie on “diagonal lines,” he realizes that marked differences in chemical behaviour might exist between the lighter and heavier elements of the group. This is the case with the four well-known members of the group. Carbon and silicon are definitely non-metallic whereas tin and lead are metals. The differences in behaviour between the two pairs of elements make it difficult to study them



together. Furthermore, tin and lead are very similar in physical and chemical properties to the transition elements. The two non-metals, carbon and silicon, will be discussed here.

## 1. CARBON

### A. OCCURRENCE

Carbon is much less abundant (0.03%) but much better known than silicon. The common substances petroleum, natural gas and limestone contain carbon. All plants and animals contain carbon in an endless variety of compounds. Carbon also occurs in nature in the free state. Coal is largely carbon with volatile impurities; graphite is mined in Ceylon and Madagascar; diamond is found mainly in the form of rough stones in deposits in the Union of South Africa, the Belgium Congo, Tanganyika, Ghana and other African countries. About 23,000,000 carats (nearly 5 tons) of diamonds are mined annually. A carat weighs 0.200 gram.

### B. ALLOTROPY (GRAPHITE AND DIAMOND)

The allotropy of carbon is most interesting. Few substances differ so greatly in physical properties (Table 28.1) as diamond and graphite, both of which are pure crystalline carbon.

**Table 28.1. Physical Properties of Pure Carbon**

<i>Property</i>	<i>Diamond</i>	<i>Graphite</i>
Configuration	Irregular sharp fragments	Flakes
Color	Colorless	Black
Light transmission	Transparent, but a high index of refraction	Opaque
Density g/cm <sup>3</sup>	3.51	2.22
Hardness	Hardest natural material known	Very soft
Conductivity	A non-conductor of electricity	A conductor (approximately 0.001 that of copper)

The uses of these two elemental forms of carbon further emphasize their contrasting properties. The diamond may be a gem in an engagement ring or in a pendant, or it may be the stylus of a record player. Fifty million dollars worth of diamonds are crushed per year for industrial uses. Small fragments are mounted in the tips of steel cutting drills and on the surface of grinding wheels for cutting steels, stones and glass. The fine dust is used for polishing the surface of fine bearing surfaces and for polishing other diamonds. Diamond is the finest abrasive known. The uses of diamond listed above depend

mainly upon the remarkable hardness of the substance and its resultant resistance to wear or scratching.

Pencil lead is a mixture of graphite and clay. The soft graphite-clay mixture wears away and leaves a black line on the paper it is rubbed against. Graphite used as a bearing lubricant may be dry, or suspended in water or oil. It forms a slippery film which reduces the friction between two sliding surfaces. Graphite with a binder is pressed into electrodes for electrolysis cells; its conductivity and its resistance to electrical corrosion make it useful.

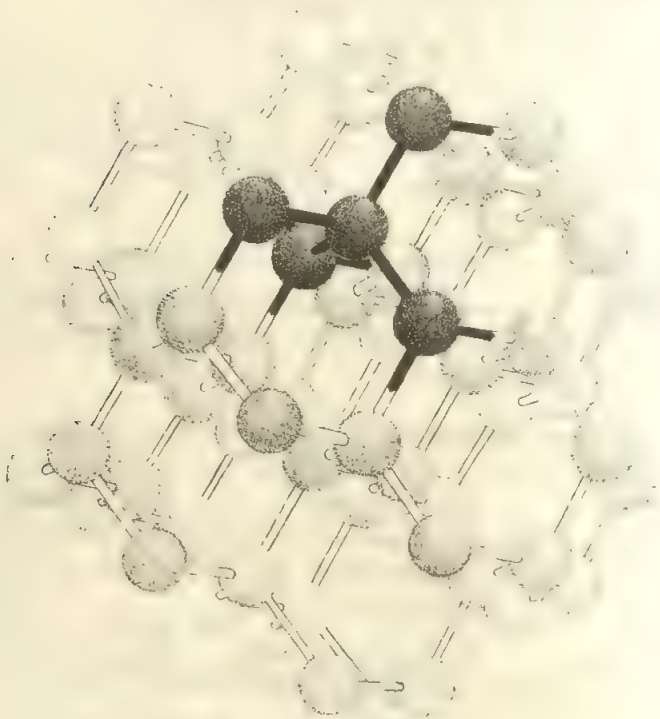


Figure 28.1. Diamond structure.

The remarkable differences in the properties of the hard glittering diamond and black, soft, flaky graphite suggest that there are great differences in the "internal" structure of the two substances. These differences can be seen if one considers the two structures as revealed by X-ray analysis. In the diamond (Fig. 28.1) each inside carbon is bonded to 4 other atoms in a three dimensional lattice. Each of the four electrons is shared with an electron from another carbon to form 4 non-polar covalent bonds.

The 4 bonds of each carbon atom repel one another and assume positions as far from one another as possible. A symmetrical structure results; the angles between any two bonds radiating from a single carbon are  $109^{\circ} 28'$ . The 4 carbon atoms to which one carbon is attached are apices of a regular

tetrahedron. Each carbon to carbon bond is 1.54 Å. One can see that this three dimensional, covalently bonded substance should be very rigid. A fracture in any direction must break many bond pairs of tightly held electrons. However, there are certain planes along which fewer bonds need be broken. To prevent shattering, a diamond cutter must determine these planes when he cleaves an uncut diamond. In such an arrangement all the valence electrons are involved in bonding between atom pairs and thus are not able to move in an electric current.

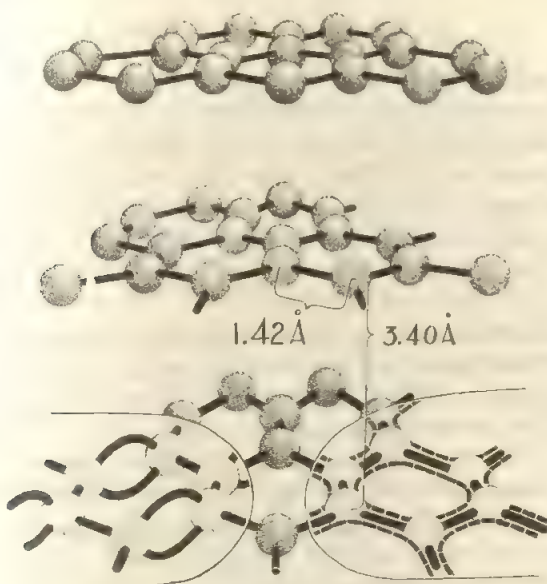


Figure 28.2. Bonding in graphite.

Graphite is not a three dimensional substance as is diamond, but each atom is bonded to three others in layers of repeating hexagons (Fig. 28.2). Each diamond may be considered a molecule, but each *layer* of graphite is a molecule. The distance between adjacent atoms in a hexagon is 1.42 Å. The distance between layers is 3.40 Å. No covalent bonds exist between the layers, leaving only 3 bonds. At first it was explained that two double (4 electrons) bonds appeared in each hexagon (Fig. 28.2, lower left). If this were true, some carbon to carbon distances would be shorter than others. However, the hexagons *are* regular. It is now believed that the extra pair of electrons for each carbon is free to move about the complete hexagon or over the entire layer, reinforcing and shortening each bond. These mobile electrons account for the electrical conductivity and for the weak bonding between layers.

There are several well-known examples of so-called "amorphous" carbon. Among these are charcoal (both from wood and bone), coke and carbon black. Charcoal is made by heating wood and bones at a high

temperature in the absence of air. Coke is the residue from a high temperature distillation of coal. Carbon black is an incomplete combustion product of natural gas formed by impinging the flame on a metal surface. Upon close investigation these forms of carbon appear to be of the graphite variety, with numerous imperfections and/or impurities. Charcoal, due to the holes in it, has a great ability to absorb matter. Activated charcoal (charcoal heated in a steam atmosphere) is added to colored solutions such as cane sugar syrup to absorb the coloring material, and is used dry in gas-absorbing masks.

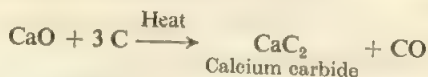
### C. PREPARATION OF DIAMOND

Free elemental carbon of the amorphous form is prepared rather easily by the methods mentioned above. Graphite may be prepared by simply heating hard coal in the absence of air in an electric furnace. The manufacture of diamonds is much more difficult. Man has sought methods for making diamonds for many years. In 1880, J. B. Hannby heated various mixtures containing graphite in iron tubes until they exploded, but no diamonds were found among the fragments. Henri Moissan dissolved carbon in molten iron then plunged the liquid metal into cold water. The tremendous pressure of the iron as it cooled from the outside and contracted was thought sufficient to press the crystallizing carbon into diamond, but only graphite flakes were found in the steel. In 1940, P. W. Bridgman placed graphite under a pressure of 6,000,000 pounds per square inch to no avail. In 1956, a team of scientists with General Electric Company subjected graphite (with other ingredients) to both extremely high temperature and extremely high pressure and produced a cluster of tiny diamonds. Diamonds sufficiently large for use in cutting tools are being made by this process and research continues to make them larger and more economically.

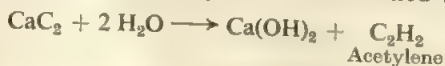
### D. SOME CARBON-CONTAINING COMPOUNDS

Many carbon-containing compounds have been discussed in previous chapters. Sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), sodium hydrogen carbonate ( $\text{NaHCO}_3$ ) and calcium carbonate ( $\text{CaCO}_3$ ) were discussed as compounds of active metals. Calcium carbonate was further discussed as a raw material for preparing mortar, aluminum and magnesium. Three other compounds should be discussed briefly here.

(1) **Calcium carbide.** When quicklime is heated with carbon to about  $3000^\circ\text{C}$ , calcium carbide is formed:

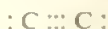


Calcium carbide is very reactive with water, yielding acetylene gas. Calcium carbide was the fuel for the old miner's lamp. Water dripping down upon the solid carbide released acetylene, which burned with a luminous flame:





The carbide ion, with a charge of  $-2$ , contains 10 electrons. Like the nitrogen molecule, it contains a triple bond.



**(2) Carbon dioxide.** Carbon dioxide, used to make sodium carbonate and sodium bicarbonate and liberated in the roasting of limestone, is also found in the respiration gases of animals. Oxygen is carried from the lungs in the blood and sugars are oxidized in the cells by this overall reaction:



Muscular energy and heat are released in the process. The carbon dioxide formed is carried in turn by the blood to the lungs where it is exhaled. Carbon dioxide is not poisonous. Its presence in air decreases the per cent oxygen and necessitates an increased rate of breathing. Animals can tolerate a 50% mixture of carbon dioxide for only a short time. However, the amount of carbon dioxide even in a closed, crowded room seldom becomes greater than 2 or 3 per cent. The high humidity that develops in such a closed space is more harmful.

Green plants in sunlight absorb carbon dioxide from the air to combine with water to form carbohydrates. The overall equation for the formation of a simple sugar is the reverse of the equation for its oxidation in the animal cell:



This reaction and others similar to it are important, because energy is taken from the sun to maintain a food-energy source, and oxygen is produced for the respiration of animals. Green plants and animals aid one another in this way. A balance must exist between them to maintain the present percentages of carbon dioxide and oxygen.

Some fire extinguishers contain liquid carbon dioxide under pressure. The liquid is vaporized upon leaving the extinguisher to form the gas. The non-flammable gas is more dense than air and covers the burning material, excluding oxygen. Other extinguishers contain sulfuric acid and sodium bicarbonate in separate, uncapped compartments. When turned over, the contents mix to form a carbon dioxide foam that covers the burning area with an inert blanket. Carbon dioxide, a product of the complete combustion of carbon-containing materials, cannot be further oxidized.

Carbon dioxide is a colorless, odorless gas with a slightly sour taste. It is very soluble in water and forms the weakly dissociated carbonic acid:



The crisp, sour taste is detected in carbonated beverages, which are saturated with carbon dioxide gas at several atmospheres pressure. When the bottle cap is removed, some gas escapes with bubbling, but enough remains to flavor the drink.

(3) **Carbon monoxide.** Carbon monoxide, an incomplete combustion product of carbon-containing materials, can be oxidized very easily to carbon dioxide:



As mentioned previously, it is a commercial fuel. Further, it is an extremely important reducing agent. One example referred to in a previous chapter was the reduction of iron oxide in the blast furnace. It is only slightly soluble in water and is a deadly poison. Breathing air containing 1% carbon monoxide will cause death in a few minutes. Carbon monoxide has a great affinity for the iron ion in the hemoglobin (the oxygen carrier) of the blood. It fills the sites normally occupied by oxygen. Without oxygen, cell metabolism ceases and death results.

Carbon monoxide will react with several metals (under the correct conditions), forming such carbonyl compounds as  $\text{Fe}(\text{CO})_5$ ,  $\text{Ni}(\text{CO})_4$  and  $\text{Co}_2(\text{CO})_8$ . One of these carbonyls,  $\text{Ni}(\text{CO})_4$ , is very important commercially. In the Mond process for producing nickel metal, carbon monoxide gas is passed over a mixture of nickel, copper and iron sulfides at  $50^\circ\text{C}$ .  $\text{Ni}(\text{CO})_4$ , a liquid, is formed, which boils at  $43^\circ\text{C}$  and is carried away as a vapor. At a still higher temperature ( $180^\circ\text{C}$ ) the carbonyl compound is decomposed: the carbon monoxide is restored and may be used again; purified nickel remains.

## 2. SILICON

### A. OCCURRENCE

Silicon is the second most abundant element in the earth's crust. It is estimated to be 27.7% silicon, 49.1% oxygen and 8.1% aluminum. Silicon and oxygen are the principle elements in earth and rocks. The continents rest on great slabs (20 miles thick) of granite which is largely silicon and oxygen. Sand is silicon dioxide. Kaolin (clay) is an impure, hydrated aluminum silicate with the approximate composition,  $\text{Al}_2(\text{Si}_2\text{O}_3)(\text{OH})_4$ . The three most abundant elements are combined together in kaolin. Other aluminosilicates are feldspar, soapstone and mica. Silicates constitute 87% of the earth's crust.

### B. COMPOUNDS OF SILICON

Silicon is a gray, metallic-appearing substance. It can be prepared by the reduction of silicon tetrachloride with an alkali metal at high temperatures:



Silicon burns in oxygen; however, the reaction is slowed by the formation of an oxide coating. Much more important than the element itself are some of its compounds.

**A. Ferrosilicon.** Silicon dissolves in many molten metals to form compounds or solid solutions. One such compound, ferrosilicon ( $\text{FeSi}$ ), is made by reducing iron silicate ores in an electric furnace. Ferrosilicon is the

source of silicon for the preparation of silicon steel. It is added to the melt in the open hearth furnace. Silicon steel is somewhat resistant to acid corrosion and possesses useful magnetic properties.

**B. Silanes.** Another metal-silicon compound, magnesium silicide ( $\text{MgSi}_2$ ), reacts with dilute hydrochloric acid in an atmosphere of hydrogen gas to produce several members of a family of compounds called silanes  $\text{SiH}_4$ ,  $\text{Si}_2\text{H}_6$ ,  $\text{Si}_3\text{H}_8$ ,  $\text{Si}_4\text{H}_{10}$ , and traces of silicon-hydrogen compounds of greater molecular weight. A model of  $\text{Si}_3\text{H}_8$  (Fig. 28.3) shows that each

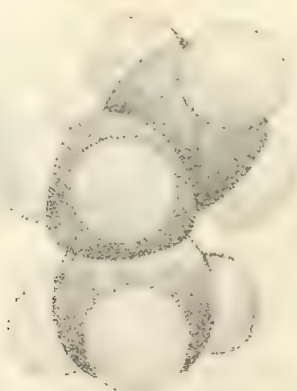


Figure 28.3. A molecule of  $\text{Si}_3\text{H}_8$ .

silicon atom in the molecule has a configuration similar to the carbon atom in the diamond crystal.

Four covalent bonds surround each silicon atom; all angles between bonds are about equal to the tetrahedral angle (in diamond),  $109^\circ 28'$ . The structural possibility of many larger silicon-hydrogen compounds of this type is apparently not important, for the silanes are not stable. They burn spontaneously in air to give silicon dioxide and water:



They react with *weak* alkali solutions to produce silicates and hydrogen.

**C. Silicon dioxide (Silica).** Sand, quartz and cristobalite are composed of silicon and oxygen in the atomic ratios of 1 to 2. The formula generally used,  $\text{SiO}_2$ , indicates that there are discrete 3 atom molecules like  $\text{CO}_2$ . But since this is incorrect, a better formula would be  $(\text{SiO}_2)_n$ , where  $n$  is a very large variable number. Each particle of sand and each quartz crystal may be considered one molecule, for the silicon and oxygen are covalently bonded together throughout the whole substance. Each silicon atom is bonded to 4 oxygen atoms. Each oxygen atom is bonded to 2 silicons. In effect, silicon atoms are bonded to one another through oxygen atoms (Fig. 28.4). This makes sand a hard substance, but not so hard as diamond, for with only 2 bonds per oxygen there are fewer covalent bonds in the crystal. As might be expected, the angles between the silicon bonds extending to the oxygens

are equal to the tetrahedral angle. The angle between the oxygen bonds is slightly less.

Silica can be fused at about  $1700^{\circ}\text{C}$  to a clear, colorless liquid. Orderly formation of the covalent bonds is difficult, and silica supercools most readily, hardening to quartz glass. Quartz glass is interesting because of its high melting point, and because of its permeability to ultraviolet light, which is excluded almost entirely by ordinary glass.

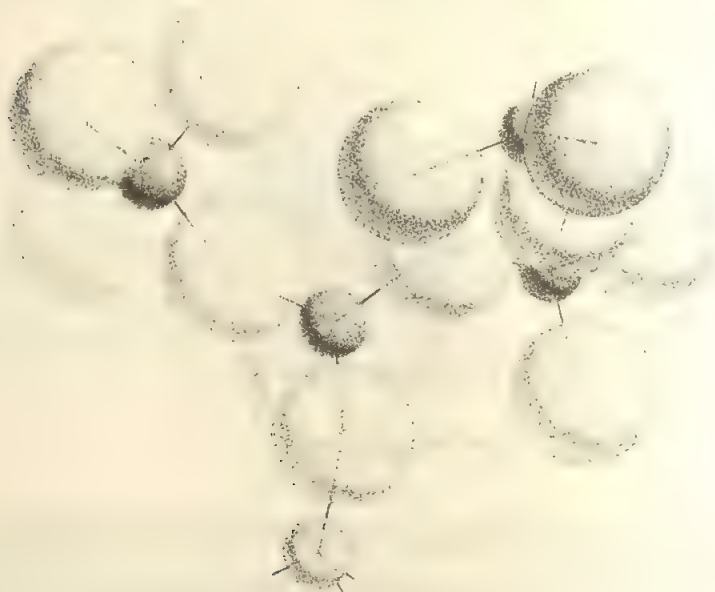


Figure 28.4. The structure of silica,  $(\text{SiO}_2)_n$ .

**D. Igneous Rocks.** The same structural unit, silicon atoms surrounded by 4 oxygen atoms in chains, exists as the basic unit in igneous rock and in clay soil produced from the rock by weathering. Granite, the most abundant rock, is 70%  $\text{SiO}_2$  combined with the elements: aluminum, magnesium, calcium, potassium, hydrogen and others. The internal structure of muscovite, a typical mineral found in granite, is illustrated in Fig. 28.5. Two silicon-oxygen layers are covalently bonded together through aluminum atoms. The double layers are bonded in turn by potassium ions. The ionic bonding is less rigid, making muscovite a flaky material. In clay the ions in the small particles of muscovite are hydrated with water molecules that wedge in between the double silicate layers, causing the clay to expand and become spongy.

**E. Glass.** Common window glass, called soft glass, is made by melting a mixture of sand, sodium carbonate and calcium carbonate. The melt of 70–80%  $\text{SiO}_2$ , 12–17%  $\text{Na}_2\text{O}$ , 5–15%  $\text{CaO}$  and 1–4%  $\text{Al}_2\text{O}_3$  is not a pure compound. It supercools to a hard brittle state with no definite crystal structure.

Pyrex glass contains a higher percentage of silicon dioxide (about 80%) and



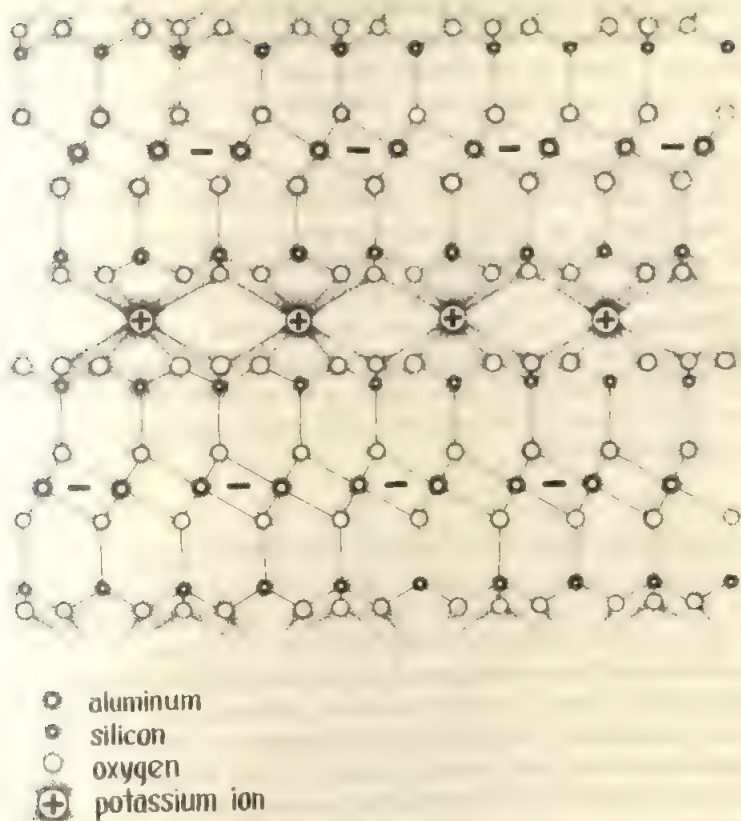


Figure 28.5. The structure of muscovite.

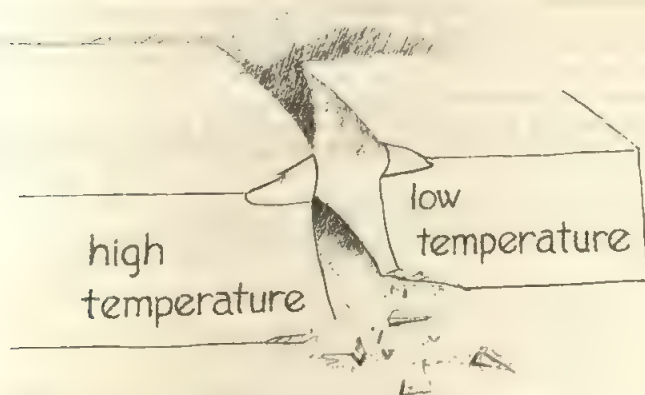
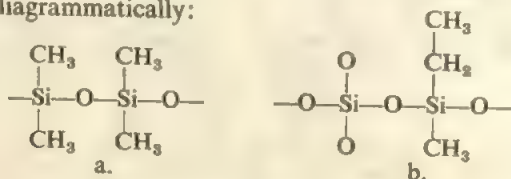


Figure 28.6. Expansion and cracking of soft glass.

12%  $B_2O_3$ , the balance being sodium and aluminum oxides. The boron-containing glass is harder and has a higher melting point than soft glass. In addition, it has a much lower coefficient of expansion. That is, it expands much less when heated. As a result, it stands much greater sudden changes in temperature. Common glass breaks when one portion is raised to a higher temperature than another, because it expands away from the cooler portion (Fig. 28.6). Because of its low coefficient of expansion, pyrex glass can be used for cooking ware.

Traces of metal oxides added to the melt color the glass. The color is somewhat dependent on the particle size of the metal oxide impurity and upon the rate of cooling, etc., of the glass. Chromium oxide and copper oxide impart a greenish color to glass; cobalt glass is blue; and gold oxide glass is ruby.

**F. Silicones.** The silicones are an interesting family of compounds containing silicon, oxygen, carbon and hydrogen. Silicon atoms are bonded to one another through oxygen atoms in long chains as in silicate rocks. However, the silicon bonds not only with oxygen but also with carbon, as shown diagrammatically:



### Characteristic Silicone Structures

If the chains of silicon and oxygen atoms are short, the substances tend to be liquid, an oil; if long, the substances are rubbery. The silicones tend to maintain their elasticity and fluidity with great changes in temperature. They are quite unreactive with most chemicals. They are used as lubricants, gaskets and electrical insulation when extreme temperature changes are encountered.

## EXERCISES

1. Of the elements C, Si, Sn and Pb, which are considered metals?
2. In the order of their abundance, list the five most abundant elements in the earth's crust.
3. List five compounds in which the two most abundant elements appear together.
4. Explain the reason for the difference in the physical properties of the two forms of elemental carbon.
5. What is a carat (in reference to diamonds)?
6. Why is there such a great difference in the densities of diamond and graphite?
7. Why should the bond angles of carbon in diamond be  $109^{\circ} 28'$ ? Why is this angle called the tetrahedral angle?
8. What are the bond angles in graphite?
9. Why is graphite a better electrical conductor than diamond?
10. In what way must a balance exist between plants and animals in the matter of respiration?
11. What is the major commercial use of carbon dioxide?
12. Why should sand be less hard than diamond?
13. What three elements are most abundant in clay soils?
14. Why does the volume of clay shrink when it sets?
15. Why should silica supercool so readily (and not crystallize) when it solidifies?
16. What is the great molecular difference between the gas  $\text{CO}_2$  and the solid  $\text{SiO}_2$ ?
17. Why is it that boron glass can stand much greater temperature changes than soft glass?
18. What is the common structural unit in silica and in silicate minerals?

ORGANIC CHEMISTRY  
AND THE ALKANES

In the preceding chapter the structural characteristics of the carbon atom in its elemental form and some of the compounds in which carbon occurs were discussed. Many additional compounds of carbon are known. In fact, it has been estimated that compounds containing carbon comprise about 90% of all the known substances. Based on this fact alone, a more intensive study of the carbon-containing compounds is justified. But the importance of carbon compounds may also be illustrated in other, more meaningful ways. For example most of the foods, most of the medicines and most of the materials used for clothing are carbon compounds. Detergents, nail polish, nylon, Orlon, DDT, plastic bottles, ethyl gasoline, tranquilizers, antibiotics and aspirin are common to everyone. All these items are compounds of carbon; all contribute in one way or another to our comfort and well-being.

Of great importance to each of us is the knowledge of the changes which substances undergo as they are used in the cells and tissues of the body. Much of the knowledge we have of biological processes has been obtained through the study of the carbon compounds, which are the principal constituents of living organisms. Historically, the principal sources of carbon compounds were plants or animals, and this early association with living organisms led to the use of the term "organic chemistry" for the field of study concerned with carbon-containing substances. As a matter of fact, organic chemistry was at one time considered to include only the study of the chemistry of living materials and their wastes. The compounds produced by and isolated from organisms were thought to differ greatly from those which could be made in the laboratory, an idea which has since been proved to be greatly in error. Today, organic chemistry includes the study of many compounds that are not found in living organisms and many that are, in fact, poisonous to them. Nevertheless, many toxic substances show structural characteristics

similar to those of the compounds which are used, transformed or produced by living organisms.

Modern characterization of organic chemistry describes it as the chemistry of carbon and its compounds, a definition based on the fact that carbon is the key element in the structures of the large number and variety of substances which are included in the classification "organic compounds." The role of carbon as the central element forming the backbone or framework of all organic substances may best be understood by a study of some of these compounds.

## 1. THE ALKANES

The simplest of the organic compounds are the hydrocarbons, compounds containing only the elements hydrogen and carbon. The simplest of the hydrocarbons are the *alkanes*. The term alkane refers to all compounds with the formula  $C_nH_{2n+2}$ , where  $n$  is any number. All compounds of this series have common and official names. Official names have the ending *-ane*. The first member of the series is methane.

### A. METHANE

Methane, the major component of natural gas, is piped from wells to be used as a fuel for domestic and industrial purposes. Its simplest formula,

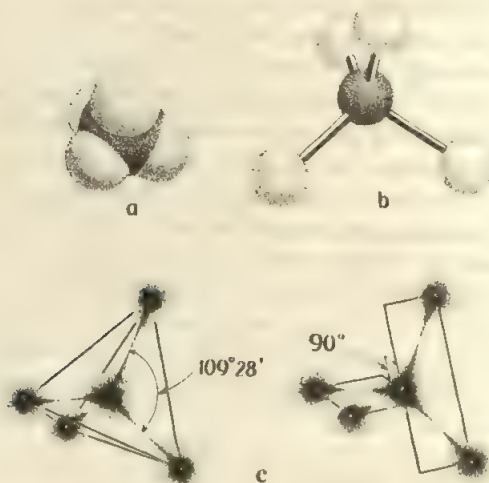


Figure 29.1. The methane molecule.

calculated from analysis, is  $CH_4$ . The molecular weight as determined from gas densities is 16. Therefore, the simplest formula is also the molecular formula. Four hydrogen atoms surround and are covalently bonded to the carbon atom. The molecule appears as shown in Figure 29.1a. The "stick"



model illustrated in Figure 29.1b shows the bonds connecting the centers of the hydrogen atoms to the carbon atom.

The carbon atom has four valence electrons. Each electron is paired with a single electron from each hydrogen to give the molecule represented

here:  $\text{H} : \overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{C}}} : \text{H}$ . The molecule is also represented by the formula  $\begin{array}{c} \text{H} \\ | \\ \text{H}-\text{C}-\text{H} \\ | \\ \text{H} \end{array}$ ,

where each line in the formula corresponds to a pair of electrons, i.e., a single covalent bond. Regardless of the formula used, however, one must always remember that the molecule is three dimensional. As in diamond, the angle between any pair of bonds is  $109^\circ 28'$ , the tetrahedral angle (Fig. 29.1c). The length of the carbon to hydrogen bond, i.e., the distance between the center of the carbon and the center of the hydrogen atom, is  $1.08 \text{ \AA}$ . Lines connecting each pair of hydrogen atoms form a regular tetrahedron. A plane passed through two of the hydrogens and the carbon atom is perpendicular to a plane passed through the carbon atom and the other two hydrogens.

With the electron configuration  $1s^2 2s^2 2p^2$  the carbon atom has four valence electrons: two in an s orbital and one in each of two 2p orbitals (Figure 29.2).

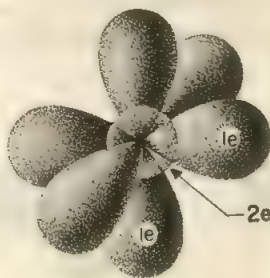
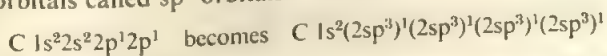


Figure 29.2.

One might expect carbon to form only two single bonds by sharing, using the 2p orbitals with the unpaired electrons. The two bonds to be formed would be perpendicular to one another. However, carbon forms four single bonds with other monovalent atoms. Methane is shown by analysis to be  $\text{CH}_4$ . All C to H bonds are identical in length and are identically related to the other three C to H bonds.

To explain this, the valence orbitals of the carbon atom are assumed to be *hybridized*. That is, the s and three p orbitals interact and produce four identical orbitals called  $sp^3$  orbitals. That is:



The  $sp^3$  orbitals thus formed are directed toward the corners of a regular tetrahedron (Fig. 29.3a).

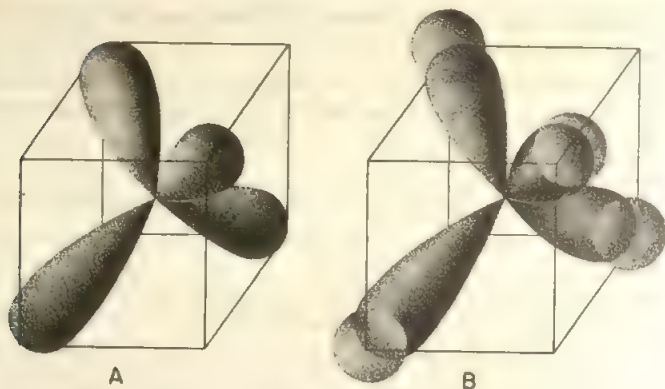


Figure 29.3.

By the overlapping of each  $sp^3$  orbital with an  $s$  orbital of hydrogen, a tetrahedral molecule is formed (Fig. 29.3b). A pair of electrons, one from the hydrogen atom and one from the carbon atom, occupies each orbital to form a bond. Each bond is symmetrical about the line connecting the centers of the two bonded atoms; because of this the bonds are called *sigma* bonds.

### B. ETHANE

The second member of the alkane series is ethane ( $C_2H_6$ ). The molecular formula used here is not completely satisfactory, since it does not indicate the

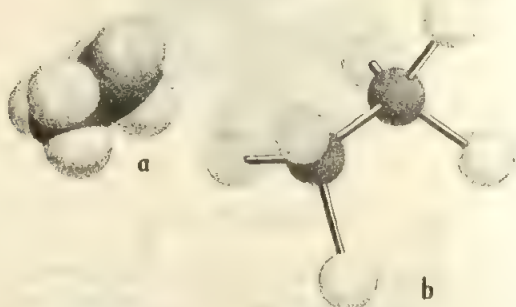
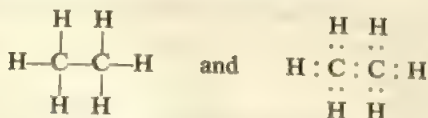


Figure 29.4. The ethane molecule.

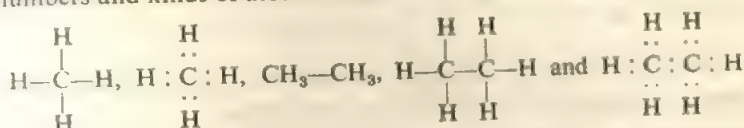
arrangement of the atoms in the molecule. A better formula is  $CH_3-CH_3$ . Still more representative formulas are:



The ethane molecule is shown in Figure 29.4. It, like methane, is three dimensional. All angles between bonds from the same carbon are  $109^\circ 28'$ .

The carbon to hydrogen bond lengths are 1.08 Å as before. The distance between the carbon to carbon centers is 1.54 Å. Like methane, ethane is a gas. It occurs as a trace in natural gas.

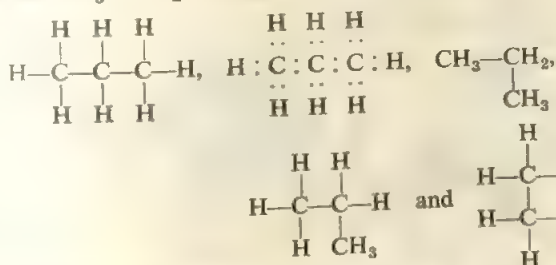
In contrast to the *molecular formulas*  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$ , which account only for the numbers and kinds of atoms in the molecule, the formulas



reveal structural features to some degree and are called *structural formulas*. Structural formulas are required because of the three-dimensional nature of carbon compounds and are very useful, since two or more substances having different properties may have the same molecular formula. Different substances which have the same molecular formulas are called *isomers*.

### C. PROPANE

The third member of the series is propane ( $\text{C}_3\text{H}_8$ ). Structural formulas for propane are  $\text{CH}_3-\text{CH}_2-\text{CH}_3$ ,



The angles between bonds are actually  $109^\circ 28'$  and not  $90^\circ$  and  $180^\circ$ , as they appear to be in the formulas. The above are all structural formulas for the

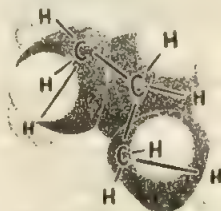


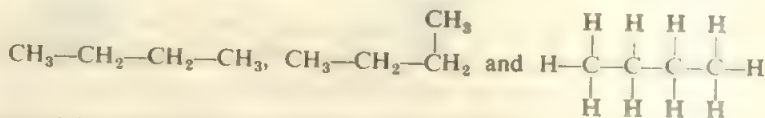
Figure 29.5. The propane molecule.

same molecule. The actual molecule is better represented as shown in Figure 29.5. The three carbons are at the apices of an isosceles triangle, and the angle between the two carbon to carbon bonds is  $109^\circ 28'$ . The carbon to carbon bond distance is the same as in ethane, as are the carbon to hydrogen distances.

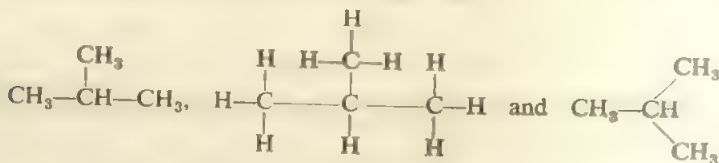
Propane is found in natural gas and in crude petroleum. A gas at room temperature and pressure, it may be liquefied under pressure. It is stored as a liquid in steel tanks. Propane is one of the so-called bottled gases used as a fuel for furnaces and ranges.

#### D. BUTANES

There are two compounds with the molecular formula  $C_4H_{10}$ . A structural formula is needed to distinguish between them.



are structural formulas for *normal butane* (Fig. 29.6a).



are formulas for *isobutane* (Fig. 29.6b).

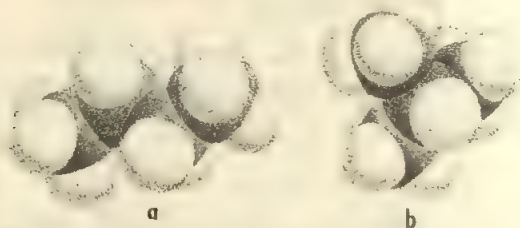


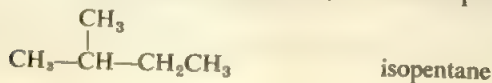
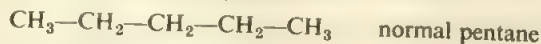
Figure 29.6. The two isomeric butanes.

“Normal” and “iso” are prefixed to the common names. “Normal” refers to “*continuous chain*” hydrocarbons, whereas “iso” is used for *branched* hydrocarbon chains and specifically for hydrocarbons with a  $CH_3$ — branch on the second carbon.

Normal butane, often written as *n*-butane, and isobutane are called isomers. Two or more different compounds having the same molecular formula, as in the present case, are *chain isomers* of one another. Normal butane and isobutane are distinctly different compounds with different properties (Table 29.2). Like propane, butane is used as a bottled gas for fuel.

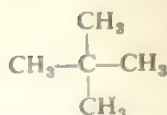
#### E. PENTANE, $C_5H_{12}$

There are three isomeric pentanes:





and



neopentane

All have the same molecular formula ( $\text{C}_5\text{H}_{12}$ ), but each has a different structure. They are different substances and are therefore isomers. The pentanes are very volatile liquids found in petroleum ethers.

Of the compounds studied, ethane,  $\text{CH}_3-\text{CH}_3$ ; propane,  $\text{CH}_3-\text{CH}_2-\text{CH}_3$ ; n-butane,  $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_3$  and n-pentane,  $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$ , are classified as continuous chain hydrocarbons. Carbons

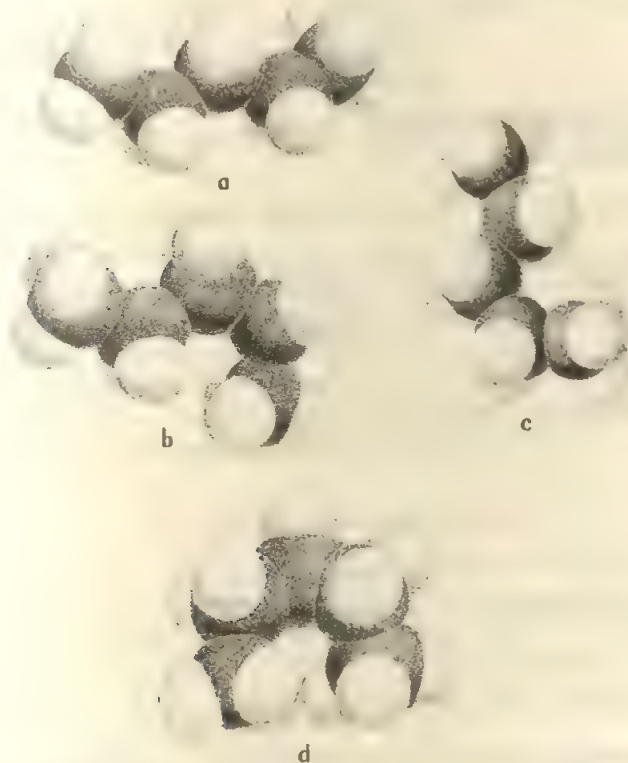
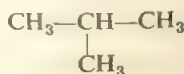


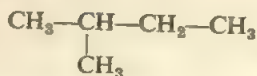
Figure 29.7. Some possible arrangements of the atoms in n-pentane.

are considered links of the chain which varies from two links to five in the compounds listed. The chains are not actually straight as they appear in the formulas. They bend through a tetrahedral angle at each carbon. At best they zigzag and may even be circular (Fig. 29.7).

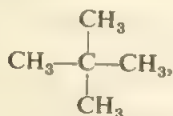
In contrast, the compounds isobutane,



isopentane,



and neopentane,

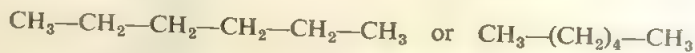


are *branched* chain hydrocarbons. The first two have but one branch; neopentane has two branches.

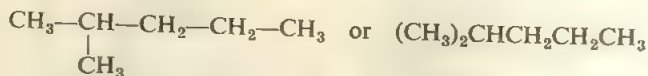
### F. HEXANES, $\text{C}_6\text{H}_{14}$

There are five isomeric hexanes:

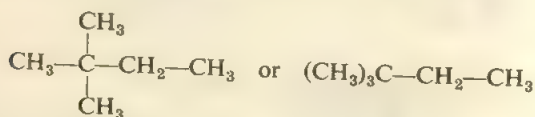
1. Normal hexane,



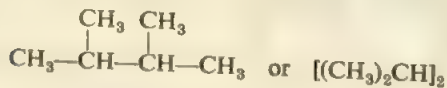
2. Isohexane,



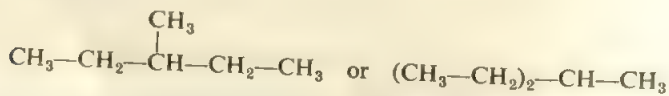
3. Neohexane (2,2-dimethylbutane),



4. 2,3-Dimethylbutane,



5. 3-Methylpentane,



All are very volatile liquids present as a mixture in the petroleum fractions called petroleum ethers (or ligroin).

### G. NUMBERS OF ISOMERS

The number of isomers increases rapidly with the number of carbons in the alkanes. Table 29.1 illustrates this point.

When four or more carbons are present, isomeric hydrocarbons can occur, because several different chain arrangements are possible. With four carbons two, and only two, structures can be made; thus only two isomers are possible. The number of possible arrangements which can be made increases rapidly with each additional carbon atom (Table 29.1).

Table 29.1. Number of Isomers

<i>Molecular Formulas</i>	<i>No. of Isomers</i>	<i>Molecular Formulas</i>	<i>No. of Isomers</i>
$\text{CH}_4$	1	$\text{C}_8\text{H}_{18}$	18
$\text{C}_2\text{H}_6$	1	$\text{C}_9\text{H}_{20}$	35
$\text{C}_3\text{H}_8$	1	$\text{C}_{10}\text{H}_{22}$	75
$\text{C}_4\text{H}_{10}$	2	$\text{C}_{14}\text{H}_{30}$	1,858
$\text{C}_5\text{H}_{12}$	3	$\text{C}_{20}\text{H}_{42}$	336,319
$\text{C}_6\text{H}_{14}$	5	$\text{C}_{30}\text{H}_{62}$	4,111,846,763
$\text{C}_7\text{H}_{16}$	9		

Relatively few of the more than four billion "isomers" of  $\text{C}_{30}\text{H}_{62}$  have been isolated. This number represents the possible arrangements of 30 carbon atoms connected to one another in chains and branches such that each carbon is connected to at least one but not more than four other carbons in a continuous network. Although some highly branched isomers would be too crowded about the center of the molecule, most of these isomers could be either isolated from petroleum or synthesized, were one to try.

## H. NOMENCLATURE

With the great number of possible isomers, it is obvious that it would be futile to have common unrelated names for each compound. For this reason the International Union of Pure and Applied Chemistry has developed a systematic method by means of which, in principle, all possible organic compounds can be named. Rules for naming alkanes by the IUPAC system are listed and applied below.

1. All normal straight chain alkanes have the name ending *-ane*. The *stem names* assigned to the first four are the common names used. The stems for the names beyond the fourth member of the series are derived from Greek.

$\text{CH}_4$	methane	$\text{n-C}_8\text{H}_{18}$	octane
$\text{C}_2\text{H}_6$	ethane	$\text{n-C}_9\text{H}_{20}$	nonane
$\text{C}_3\text{H}_8$	propane	$\text{n-C}_{10}\text{H}_{22}$	decane
$\text{n-C}_4\text{H}_{10}$	butane	$\text{n-C}_{11}\text{H}_{24}$	undecane
$\text{n-C}_5\text{H}_{12}$	pentane	$\text{n-C}_{12}\text{H}_{26}$	dodecane
$\text{n-C}_6\text{H}_{14}$	hexane	$\text{n-C}_{13}\text{H}_{28}$	tridecane
$\text{n-C}_7\text{H}_{16}$	heptane	$\text{n-C}_{14}\text{H}_{30}$	tetradecane





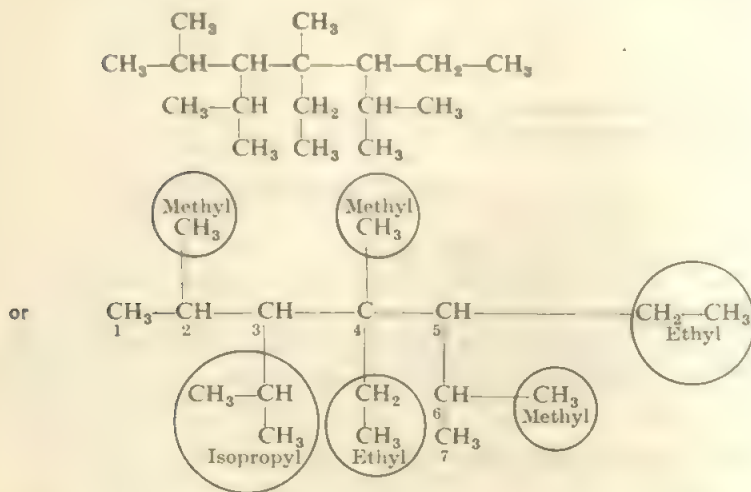


The chain is numbered (from the right), because the sum of the numbers used in the name is then only  $6 + 3 + 4 + 4 + 6 = 23$ .

If Compound D were numbered from the left, the name would be 4-ethyl-4,6,6,7-tetramethylnonane; and the sum of the numbers appearing in this name is  $4 + 4 + 6 + 6 + 7 = 27$ .

Naming from the "most branched end" gives the set of numbers with the *smaller sum*.

### Compound E:



may be named either:

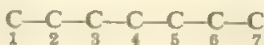
4,5-diethyl-3-isopropyl-2,4,6-trimethylheptane or 3,4-diethyl-5-isopropyl-2,4,6-trimethylheptane.

(The numbering of carbons in the main chain was reversed to form the second name. Both names are acceptable, because the sum of the numbers appearing in the name is the same (24) for each name.) Notice that the terms with their prefixes appear in the name in alphabetical order.

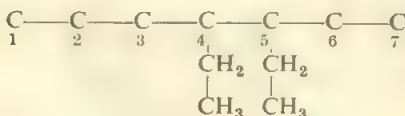
*Reconstruction* of the formula from the name may assist in understanding the system of nomenclature.

4,5-diethyl-3-isopropyl-2,4,6-trimethylheptane

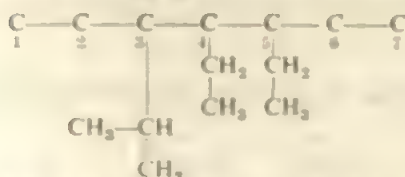
a. is a heptane:



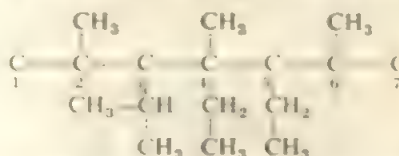
b. with two ethyl groups, one attached to carbon 4 and one to carbon 5:



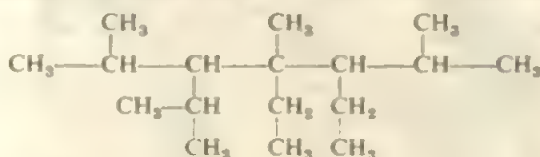
c. with an isopropyl group on carbon number 3



d. and with three methyl groups, one each on carbons 2, 4 and 6:



e. Hydrogen "groups" are added until each carbon has 4 bonds



One should recognize that this formula and formula E represent identical compounds.

Compound E may be named in a slightly different way that illustrates extension of the IUPAC system to even more complicated compounds:

4,5-diethyl-3-(1-methylethyl)-2,4,6-trimethylheptane.

## I. PHYSICAL PROPERTIES OF THE ALKANES

Properties of substances are determined in varying degree by a number of factors. The composition, the bond type, the polarity or non-polarity, the molecular weight, the size, and the shape or configuration of a molecule are among the most important.

The alkanes, being composed solely of carbon and hydrogen (elements of nearly the same electronegativity), with the hydrogens being arranged in a more or less symmetrical way about the carbons, are essentially non-polar. Therefore, they are insoluble in water. Water molecules, being strongly polar, cling together and do not permit the alkane molecules to come between them. On the other hand, alkanes are soluble in non-polar solvents, such as benzene, ether, carbon tetrachloride, and other petroleum products.

The density of substances depends mostly on the kinds and ratios of atoms in the molecule. Each kind of atom has almost the same size in all compounds and possesses constant mass. The smaller members of the alkane series have a higher ratio of the lighter hydrogen atoms (in methane, 4 to 1) and are therefore less dense. The hydrogen to carbon ratio decreases to a limiting value of almost 2 to 1 with higher molecular weight alkanes, and the density

risers to an almost constant value of 0.777 g/ml (Table 29.2). Because they have a density less than that of water, alkanes form a film; or "oil slick," on the surface of water.

**Table 29.2. Physical Properties of Selected Paraffin Hydrocarbons**

Name	Formula	Melting Point, °C	Boiling Point, °C	Density at 20 °C
Methane	CH <sub>4</sub>	-182.5	-161.5	0.424 (at bp)
Ethane	C <sub>2</sub> H <sub>6</sub>	-183.2	-89	0.546 (at bp)
Propane	C <sub>3</sub> H <sub>8</sub>	-187.7	-42.1	0.582 (at bp)
Butane	C <sub>4</sub> H <sub>10</sub>	-138.3	-0.55	0.5787
Isobutane	C <sub>4</sub> H <sub>10</sub>	-159.4	-11.7	0.5572
Pentane	C <sub>5</sub> H <sub>12</sub>	-129.7	36.0	0.6262
2-Methylbutane	C <sub>5</sub> H <sub>12</sub>	-159.9	27.9	0.6197
2,2-Dimethylpropane	C <sub>5</sub> H <sub>12</sub>	-15.9	9.5	0.5904
Hexane	C <sub>6</sub> H <sub>14</sub>	-95.4	68.6	0.6594
Heptane	C <sub>7</sub> H <sub>16</sub>	-90.6	98.4	0.6838
Octane	C <sub>8</sub> H <sub>18</sub>	-56.8	125.6	0.7028
Nonane	C <sub>9</sub> H <sub>20</sub>	-53.7	150.7	0.7181
Decane	C <sub>10</sub> H <sub>22</sub>	-29.7	174.0	0.7299
Undecane	C <sub>11</sub> H <sub>24</sub>	-25.6	195.8	0.7403
Dodecane	C <sub>12</sub> H <sub>26</sub>	-9.6	216.3	0.7488
Tridecane	C <sub>13</sub> H <sub>28</sub>	-6.2	235.5	0.7467
Tetradecane	C <sub>14</sub> H <sub>30</sub>	5.5	252.5	0.744 (at mp)
Pentadecane	C <sub>15</sub> H <sub>32</sub>	10	270.5	0.776 (at mp)
Hexadecane	C <sub>16</sub> H <sub>34</sub>	18	287.5	0.775 (at mp)
Octadecane	C <sub>18</sub> H <sub>38</sub>	28	317	0.777 (at mp)
Nonadecane	C <sub>19</sub> H <sub>40</sub>	32	330	0.777 (at mp)

As with any series of similar substances, the boiling point increases regularly with increasing molecular weight. However, as expected, the boiling points are much lower for these non-polar compounds than for polar compounds with corresponding molecular weights. For example, compare the boiling point of methane (-161.5°C) with that of water (100°C). Table 29.2 shows the regular increase in boiling point with successive addition of —CH<sub>2</sub>— units in the normal alkanes, a so-called *homologous series*.

The n-alkanes make up a *homologous series*, since each member of the series differs by one —CH<sub>2</sub>— unit in the carbon chain from the preceding or following member, and all members of the series may be represented by the formula CH<sub>3</sub>—(CH<sub>2</sub>)<sub>n</sub>—H, where n is zero or any number. Neighboring compounds are homologs of each other. As seen in Table 29.2, the boiling point increases with the addition of each —CH<sub>2</sub>— unit. The increase in the boiling point from compound to compound is larger for the smaller members, but it becomes almost constant at 13°C per —CH<sub>2</sub>— added with the higher members.



The boiling point is also affected by changes in structure. Isomeric alkanes exhibit differences in boiling points. In the *n*-alkane series the boiling point increases with each added  $\text{—CH}_2\text{—}$  group, not only because of an increase in molecular weight, but because longer molecules can wrap around and become entangled with one another and are thus more difficult to separate. In Table 29.3 the boiling point of *n*-hexane, for example, may be compared with its more branched and more compact isomers, 2-methylpentane, 3-methylpentane, 2,3-dimethylbutane and 2,2-dimethylbutane (Fig. 29.8). The more branched structures have the lower boiling points.

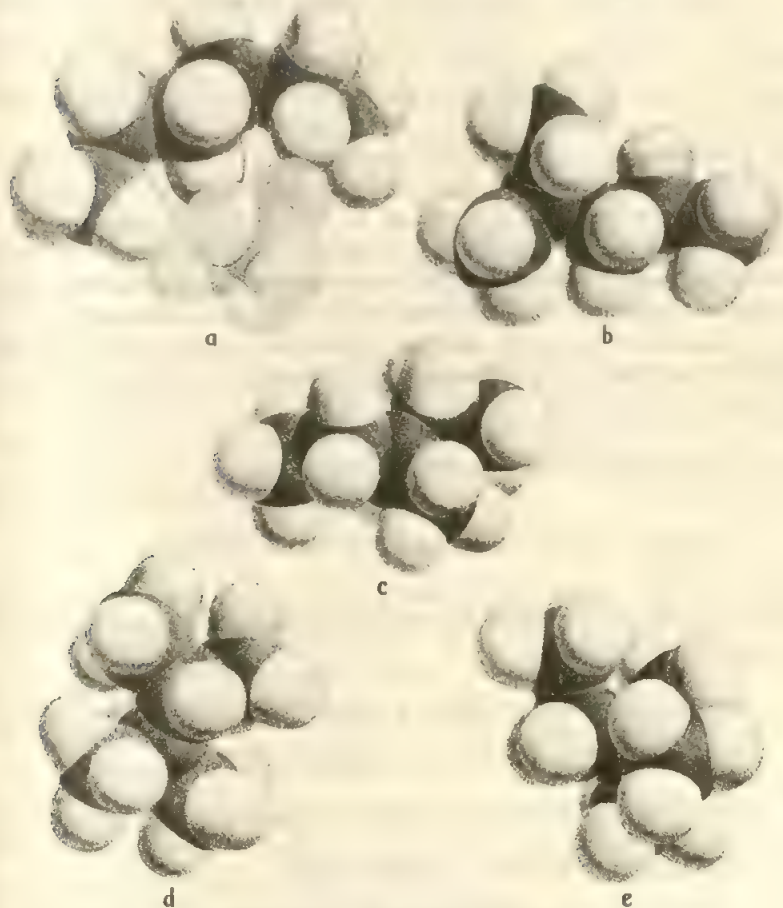


Figure 29.8. The isomeric hexanes.

**Table 29.3. Boiling Points of the Isomeric Hexanes**

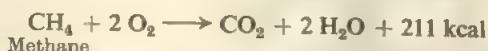
<i>n</i> -hexane	68.7°C
3-methylpentane	63.3
2-methylpentane	60.3
2,3-dimethylbutane	58.0
2,2-dimethylbutane	49.7

The viscosity, a measure of the difficulty with which molecules slide by one another, increases with chain length so that the members of the series vary from free flowing liquids to thick oils. The liquids tend to be oily to the touch. The high molecular "solids" are waxy solids. All are nonconductors of electricity.

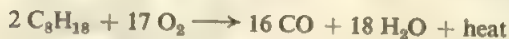
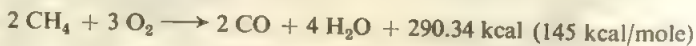
### J. CHEMICAL PROPERTIES OF THE ALKANES

The alkanes are singularly unreactive organic compounds. Because they are unaffected by most bases, acids and mild oxidizing agents, they have been named paraffins (that is, substances having little affinity). The name paraffin is employed specifically for a waxy mixture of high molecular weight alkanes, paraffin wax. The relative unreactivity of the alkanes with various reagents is apparently due to the fact that stable carbon to carbon or carbon to hydrogen bonds must be first broken before reaction can occur.

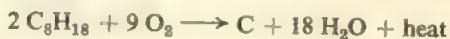
**(1) Combustion.** Alkanes will combine with either pure oxygen or oxygen in the air. However, this does not occur without "ignition." A small volume of the alkane vapor-air mixture is heated locally with an electric spark or flame. Because of the locally high temperature, some of the activated (or heated) molecules collide with sufficient velocity to break bonds and start the reaction. The heat liberated on combustion heats other molecules to reaction temperature, and the combustion reaction continues. The reaction of an alkane with an ample supply of oxygen yields carbon dioxide and water.



With insufficient oxygen the following reactions occur simultaneously with those above.



and



One can see that burning with insufficient oxygen will cause the formation of either poisonous carbon monoxide gas or flakes of soot (carbon), which when heated to incandescence in a flame emit a yellow light. Such side reactions will release many fewer calories per molecule of hydrocarbon gas burned. *Complete* combustion of one gram-molecular weight (mole) of methane yields 211 kcal, *incomplete* combustion to carbon monoxide gives 145 kcal, and *incomplete* combustion to carbon gives 118 kcal.

The heats of complete combustion for members of the homologous n-alkane series are tabulated in Table 29.4.

**Table 29.4. Heats of Combustion per Mole in n-Alkane**

	<i>Kilocalories per Mole</i>		<i>Heat per Added —CH<sub>2</sub>— Group</i>	<i>Average Increase per Added —CH<sub>2</sub>—</i>
	<i>Gases</i>	<i>Liquids</i>		
CH <sub>4</sub>	210.8			} 156.4 kcal/mole
C <sub>2</sub> H <sub>6</sub>	368.4		157.6	
C <sub>3</sub> H <sub>8</sub>	526.3		157.9	
n-C <sub>3</sub> H <sub>12</sub>	838.3	833.4	156.0	
n-C <sub>4</sub> H <sub>14</sub>		989.8	156.4	
n-C <sub>5</sub> H <sub>18</sub>		1149.9	160.0	
n-C <sub>6</sub> H <sub>18</sub>		1203.7	152.8	
n-C <sub>10</sub> H <sub>22</sub>		1610.7	154.0	

One can see that the addition of a —CH<sub>2</sub>— group in the chain increases the heat of combustion by a nearly constant factor (156 kcal per mole) as expected.

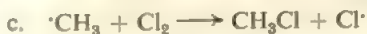
(2) **Halogenation.** Alkanes will react with the halogens (chlorine, bromine, and iodine), but only in sunlight or in artificial ultraviolet light. Absorption of an ultraviolet light photon by the halogen molecule gives it sufficient vibration energy to split. The mechanism of the reaction between chlorine and methane is as represented:



The active chlorine atom (called a free radical) then attacks a methane molecule and takes a hydrogen atom:



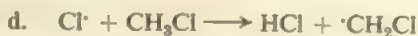
The methyl free radical,  $\cdot\text{CH}_3$ , attacks another chlorine molecule:



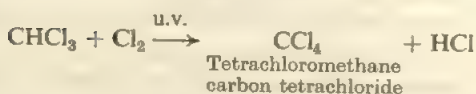
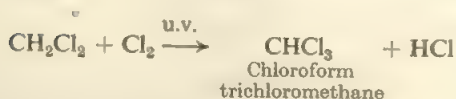
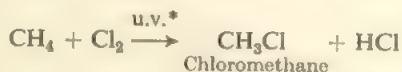
yielding methylchloride (chloromethane) and another chlorine atom. The chlorine atom may react again as in equation b, yielding  $\text{CH}_3^\cdot$  to react as in c. Reactions b and c, which follow one another over and over again, are called chain reactions. They are alternate links, one following another in a chain. One can see that because of the chain a small amount of absorbed light may cause extensive reaction.

This type of reaction,  $\text{CH}_4 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{HCl}$ , is called *substitution*. Regardless of the intermediate steps (mechanism), the final result is the replacement or substitution of a chlorine for a hydrogen atom in the methane molecule. Further substitution by a halogen can and does occur. The atomic halogen formed either by absorption of light or by step c (above) in the chain

reaction may attack a  $\text{CH}_3\text{Cl}$  molecule, as well as a methane, with the following result:

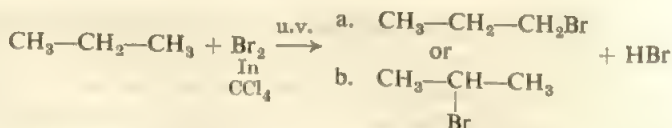


In this manner 4 hydrogens of methane may be replaced by 4 chlorine atoms. The sequence of reactions is as follows:



Unless an excess of chlorine gas is used, a mixture of the mono-, di-, tri- and tetrahalogenated methanes is obtained in the reaction. However, if the reaction is conducted for an extended period with an excess of chlorine gas, the completely substituted methane, tetrachloromethane, may be obtained as the only product.

Halogenation of other alkanes occurs in a manner analogous to that of methane, but a greater variety of products is possible. Consider the bromination of propane. Propane gas is bubbled through a solution of bromine in the inert solvent carbon tetrachloride during illumination with ultraviolet light. The halogen and alkane are both quite soluble in the non-polar solvent and are brought together for reaction.



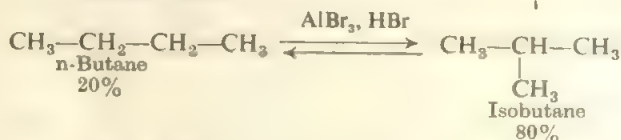
When one molecule of bromine reacts with one of propane, one of two products are possible: (a) 1-bromopropane and (b) 2-bromopropane. Having the same molecular formula ( $\text{C}_3\text{H}_7\text{Br}$ ), the two are isomers. Both isomers

\* u.v. is an abbreviation for ultraviolet light.





(5) **Isomerization.** Despite the inertness of the alkanes, they react readily in the presence of certain catalysts. As an example, *n*-butane in the presence of aluminum bromide and hydrogen bromide is converted to 80% isobutane



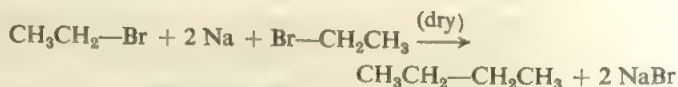
With the same catalysts, pure isobutane is converted to the same percentage mixture, 20% *n*-butane and 80% isobutane, hence the double arrow.

The same type reaction occurs with higher molecular weight alkanes. Chain fragments are broken off and reattached on the chain. The point of attachment is not predetermined and an equilibrium mixture (often very complex) may eventually be obtained. The usual effect is to increase the percentage of highly branched isomers.

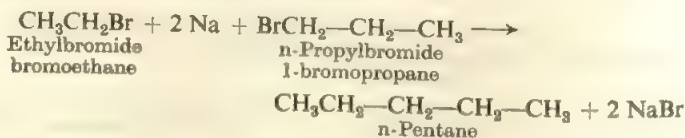
### K. PREPARATION OF ALKANES

As will be discussed later, most alkanes are used as mixtures of compounds of nearly the same molecular weight and nearly the same boiling point. These mixtures may, however, be separated into pure compounds. To obtain an individual alkane in pure form it is often simpler to synthesize it than to attempt its separation and purification from a naturally occurring mixture (petroleum). One relatively simple and useful reaction for synthesizing pure alkanes is the Wurtz reaction.

(1) **Wurtz Reaction.** Reaction occurs when a dry alkyl halide (halogen-substituted alkane) is added slowly to small pieces of sodium metal. The reaction with bromoethane is illustrated below:



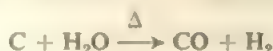
This reaction is most useful when only a single alkyl halide (here bromoethane) is used such that two identical hydrocarbon fragments ( $\text{CH}_3\text{CH}_2\text{—}$ ) are joined together. It is possible to make unsymmetrical alkanes, that is, alkanes that are not made of two identical halves. For example, ethyl bromide and *n*-propylbromide (1-bromopropane) combine with the elimination of bromine in the presence of sodium to give *n*-pentane.



As one might expect, the yield is low; *n*-butane and *n*-hexane are formed also.

(2) **Fischer-Tropsch Synthesis.** The best source of alkane fuels for countries that do not have petroleum resources is the Fischer-Tropsch synthesis. By this process coal, steam and hydrogen can be converted to a

mixture of alkanes. Coal is converted to carbon monoxide by the water-gas reaction (page 163).



The water-gas mixture is enriched with more hydrogen and passed over a cobalt-thoria catalyst at about 250°C to give a mixture of alkanes somewhat like crude petroleum. For preparation of octane, the reaction is:

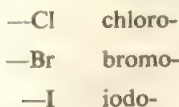


### L. ADDITIONAL NOMENCLATURE

In the discussion of the reactions of alkanes, several *substituted* alkane products were named with no attendant explanation. One such compound was the bromosubstituted alkane:

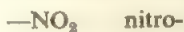


One may think of the compound as propane with bromine atoms substituted for hydrogens. The IUPAC name, 1,2-dibromopropane, is a logical extension of the naming system as used for branched alkanes. The group is named and its position on the chain noted by a number preceding it. To extend the system to include alkanes with substituted groups, one needs to know the group names. As new groups are studied, they will be named. The non-alkyl groups encountered thus far are the halogens:

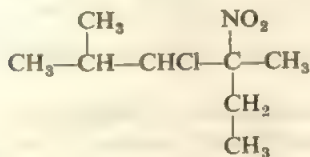


(Any one of these may be represented by —X or halo- [for halogen].)

and the nitrogen dioxide group



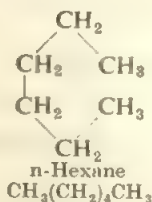
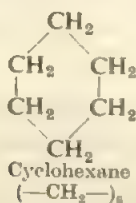
The correct IUPAC name for the substituted alkane:



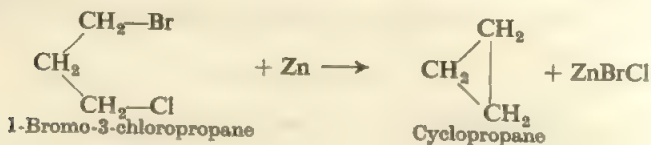
is 3-chloro-2,4-dimethyl-4-nitrohexane. The compounds  $\text{CH}_3\text{CH}_2\text{Br}$ ,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$  and  $\text{CH}_3\text{CHBrCH}_3$  are *properly* called bromoethane, 1-bromopropane, and 2-bromopropane, respectively, but they are more often labeled simply ethylbromide, n-propylbromide and isopropylbromide.

## M. CYCLOALKANES

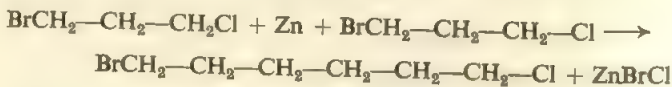
One important item remains, the introduction to the series of alkanes called the cycloalkanes. Each of these compounds may be represented by the molecular formula  $C_nH_{2n}$ , where  $n$  is any number from 3 to 30 for known compounds. Each compound has 2 fewer hydrogen atoms than the open chain alkane with the same number of carbons. The simplest of these compounds may be represented by the structural formula  $(-CH_2-)_n$ , where  $n$  has the same values as in the molecular formula. At first glance one sees that there are no terminal groups (end of the chain groups,  $-CH_3$ ). This fact both accounts for the 2 fewer hydrogens and predicts the general configuration of the compounds. Since all groups are non-terminal  $-CH_2-$  groups, the compounds have no end. They are cycloalkanes ("circle" alkanes). Compare cyclohexane and *n*-hexane:



Cyclopentane,  $(CH_2)_5$ , and cyclohexane,  $(CH_2)_6$ , occur naturally. Both are very volatile liquids found in crude petroleum. All the cycloalkanes can be formed in varying yields by treating the proper dihaloalkanes with zinc dust. Cyclopropane is prepared from 1-bromo-3-chloropropane.



These are *intramolecular* (within the molecule) reactions. The yield of the reaction is decreased greatly because *intermolecular* (between molecules) reaction also occurs:



In practice the intermolecular reaction is minimized by using a very dilute solution of the dihalide in some inert solvent. In this situation the two ends of the same molecule have more time to meet and react before colliding with another molecule.

Cyclopropane, like normal propane, is a gas. It is widely used as a general anesthetic in place of ether. Cyclobutane is also a gas, whereas cyclopentane and cyclohexane are volatile liquids.



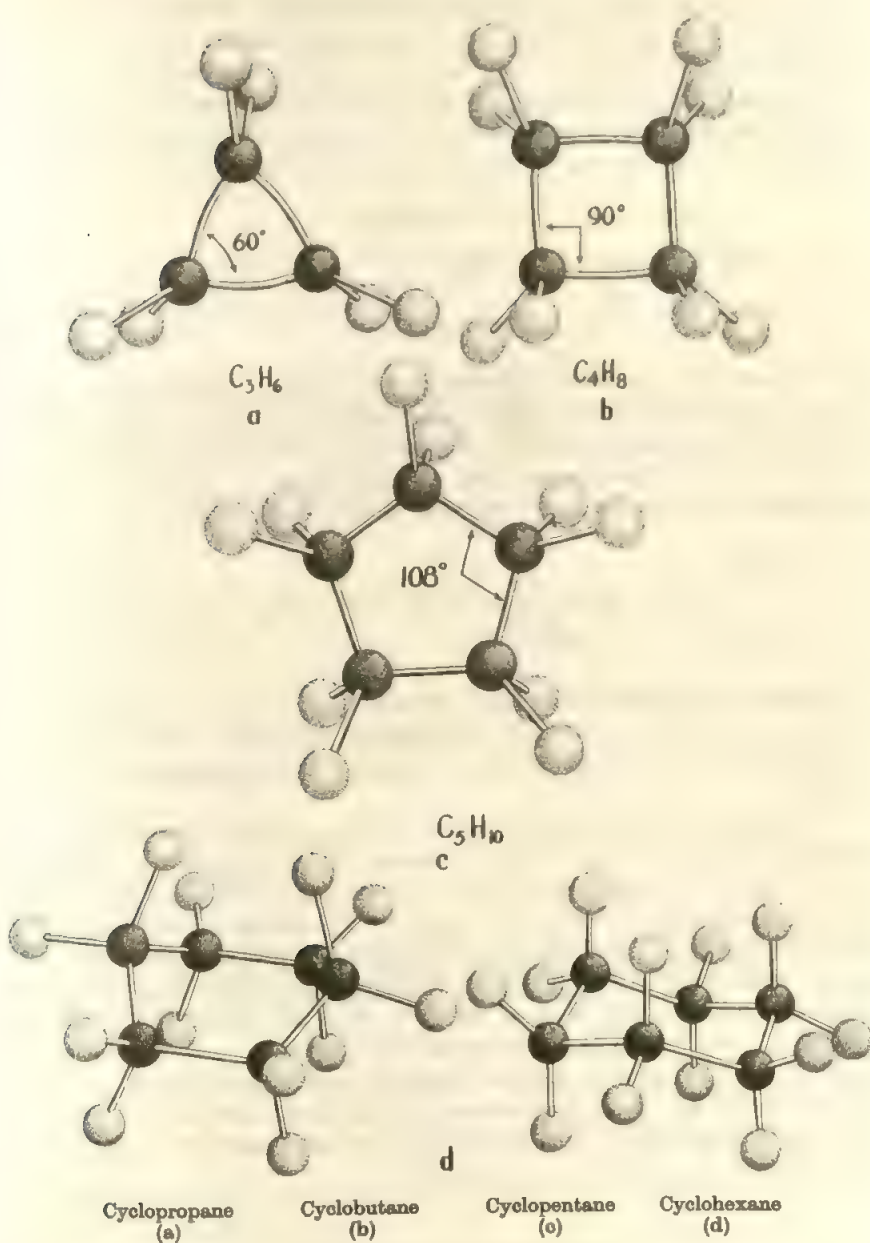
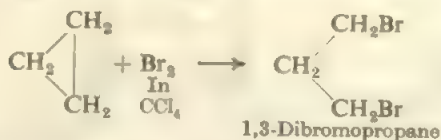


Figure 29.9. Configuration of cycloalkanes.

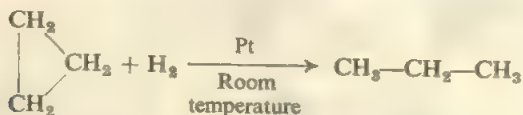
All the carbons in the above compounds are "saturated," i.e., they have 4 single bonds. With the exception of cyclopropane and, to a lesser degree, cyclobutane, the  $-\text{CH}_2-$  groups act just like  $-\text{CH}_2-$  groups in open chain alkanes. The compounds are very inert, being limited in reactions to halogenation with sunlight, combustion and vapor phase nitration.

In contrast, cyclopropane reacts readily with sulfuric acid, hydrobromic acid and bromine, *the latter in the dark*. The reactions are *additions* and *not substitution*. With bromine in carbon tetrachloride the reaction is:



As cyclopropane is bubbled into the colored bromine solution the solution becomes lighter and lighter in color. The colorless dibromo compound which is formed remains in the solvent to be separated by fractional distillation.

Furthermore, cyclopropane can be hydrogenated when mixed with hydrogen under pressure in the presence of finely divided platinum:



The other cycloalkanes can be hydrogenated, but not under the same conditions. Cyclobutane requires a temperature of  $120^\circ\text{C}$ , whereas  $200^\circ\text{C}$  is required to saturate and convert cyclopentane and cyclohexane to normal alkanes.

The greater reactivity of cyclopropane (and cyclobutane) with the addition of reagents has been ascribed to a straining of the bonds in the molecule. Johann Friedrich von Baeyer (1835–1917) reasoned that since the normal carbon bond angle is the tetrahedral angle  $109^\circ 28'$ , the bonds in cyclopropane and cyclobutane are strained. The bond angles in cyclopropane are  $60^\circ$ ; in cyclobutane,  $90^\circ$  (Fig. 29.9a and b). Therefore, according to the Baeyer strain theory there is an overall strain of  $109^\circ 28' - 60^\circ = 49^\circ 28'$  and  $109^\circ 28' - 90^\circ = 19^\circ 28'$ , respectively, in cyclopropane and cyclobutane. These two molecules tend to open up. On the other hand, the angles in cyclopentane are  $108^\circ$  (very little strain). If the cyclohexane ring is planar (all carbons lie in 1 plane) the angles would be  $120^\circ$ , but because the ring can "buckle," the angles are  $109^\circ 28'$ , and there is no strain (Fig. 29.9).

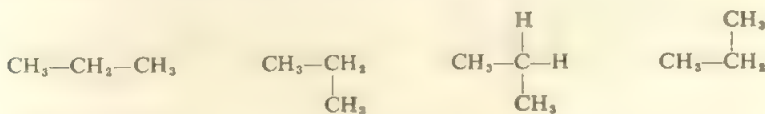
## IN SUMMARY

In organic compounds a great new field of chemistry begins to unfold, a field containing more than 90% of all known chemical compounds, a field where the covalent bond dominates, a field with both simple and complex

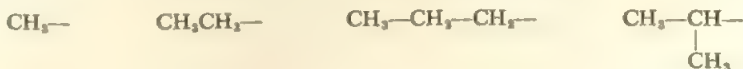
structures. A new system of nomenclature has been introduced, and, although it has been applied to only a few compounds, it will be expanded to cover all of them. One can best learn the method by naming many examples. Many new terms have been introduced, and one can hardly speak of organic chemistry without a knowledge of these terms, which have been collected in Exercise 1 below. The chemistry of the alkanes has been discussed. The student should commit to memory the preparations, reactions and general properties of these compounds.

## EXERCISES

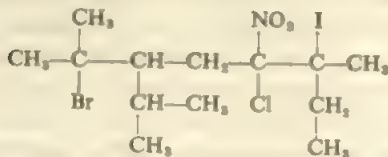
- Define each of the following terms and illustrate each *italicized* term with an example:
  - organic chemistry
  - organic chemical (*compound*)
  - hydrocarbon
  - alkane
  - simplest formula (use isobutane for an example)
  - molecular formula (use isobutane for an example)
  - structural formula (use isobutane for an example)
  - the tetrahedral angle
  - continuous chain hydrocarbon
  - covalent bond
  - branched hydrocarbon
  - isomers
  - alkyl group
  - polar compound
  - boiling point
  - homologous series
  - homolog
  - n-alkane
  - isoalkane
  - paraffin
  - kcal.
  - substitution reaction
  - haloalkane
  - pyrolysis
  - isomerization
  - Baeyer strain theory
  - cycloalkane
  - planar
- What is the distance between (a) centers of adjacent carbons (C—C) in an alkane and (b) centers of a hydrogen atom and the carbon to which it is attached (C—H)?
- Which formula represents the structure of propane best?



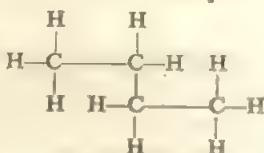
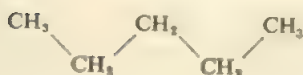
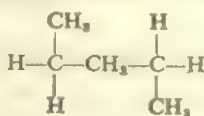
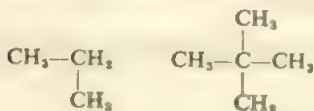
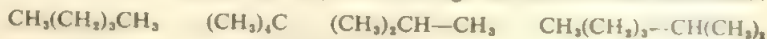
- Write structural formulas for each of the isomeric hexanes and name each one with the correct IUPAC name.
- Name each of these alkyl groups:



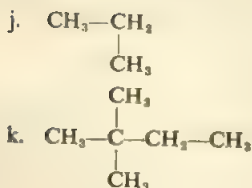
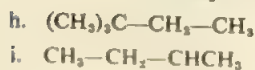
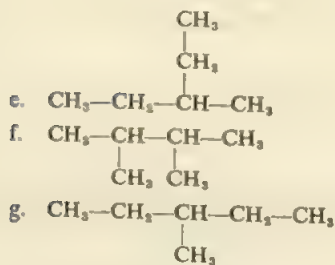
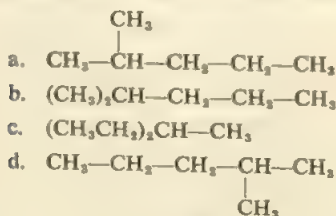
6. Name each group attached to the main chain of this compound (list them in alphabetical order):



7. Which of the compounds represented by the following formulas are branched alkanes?



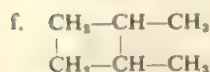
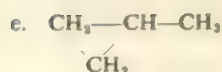
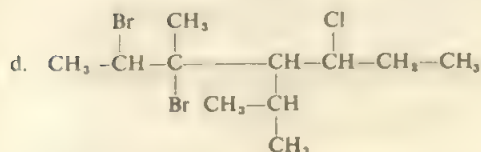
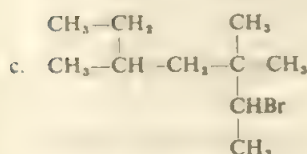
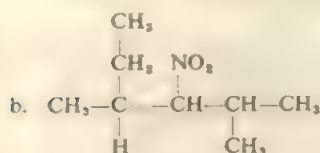
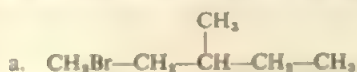
8. How many (different) isomers of n-hexane are represented here?







9. How is the insolubility of alkanes in water related to their relatively low boiling points?
10. Write balanced equations for the complete combustion of propane, n-butane and n-heptane.
11. Chlorine gas is permitted to react with propane in the presence of ultraviolet light. Write structural formulas for and name each possible compound formed.
12. Write equations illustrating each of the following (include reaction conditions over the arrow):
- halogenation of methane
  - nitration of ethane
  - cracking of tetradecane
  - isomerization of n-octane
  - complete combustion of methane
  - incomplete combustion of ethane
13. Sodium metal is dropped into a mixture of bromomethane, bromoethane, 1-bromopropane, and 2-bromopropane. Draw the structures and name all the possible products, using the IUPAC system.
14. Why is cyclopropane more reactive with halogens than propane? Why is the reaction of cyclopropane with bromine in the dark called addition?
15. Write the correct IUPAC name for each compound whose structure is given.



16. Name three homologs of n-propane.

# MULTIPLE CARBON TO CARBON BONDS

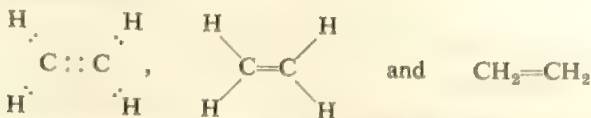
## 1. INTRODUCTION

Hydrocarbons were introduced in the previous chapter by the discussion of one type, the alkanes. *Alkanes* are composed of carbon atoms linked together in continuous or branch chains by *single covalent bonds*, with hydrogen added until there are 4 single bonds on each carbon. Two other ways of linking carbon atoms are possible, by double and triple bonds. The presence of either of these multiple bonds endows the hydrocarbon with new and unique properties. A *structural* feature or a group that gives a compound different properties is called a *functional group*. This chapter is largely a study of the two functional groups, the double and triple carbon to carbon bonds, and of the compounds that contain them.

## 2. NATURE OF THE MULTIPLE BONDS

### A. THE DOUBLE BOND

Ethylene ( $C_2H_4$ ) is the simplest hydrocarbon containing a double bond. Its structural formulas are:



It is obvious that each atom of the molecule has gained the inert gas configuration by sharing. Models of the ethylene molecule appear in Figure 30.1. Figure 30.1a is a model of the molecule, showing the positions and relative sizes of the atoms. Figure 30.1b and c are attempts to describe the bonding involved. In b, two of the bonds of each carbon are bent together from the

tetrahedral angle between them to make parallel single bonds. However, both portions of the double bond would be identical; both pairs of electrons would occupy similar orbitals. Recent mathematical studies of bond orbitals

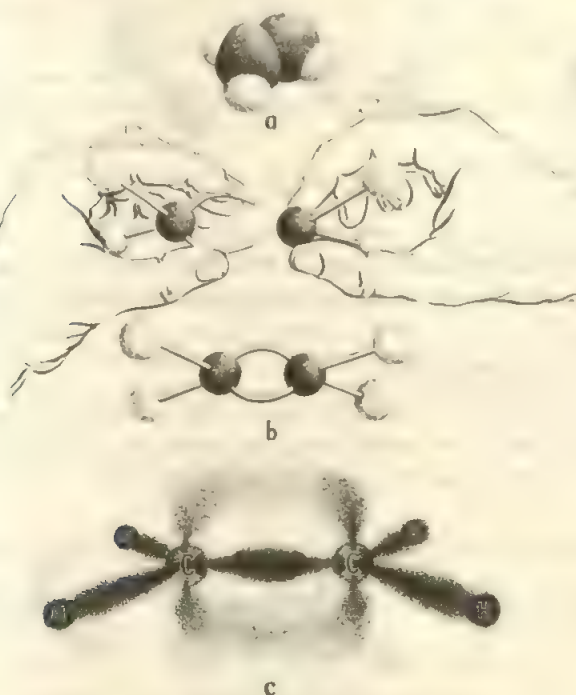


Figure 30.1. Models of ethylene.

have suggested the type of bonding represented in Figure 30.1c. Each carbon forms a single electron pair bond with two hydrogens. These C—H bonds are similar to the C—H bond in alkanes. The double bond in ethylene is composed of two parts, a sigma bond and a pi bond. The isolated atoms have four electrons in the valence level (Fig. 30.2):

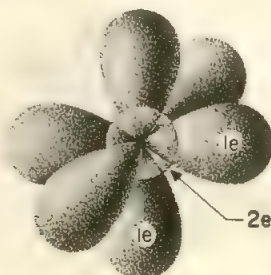


Figure 30.2.

To form the bond required in ethylene three orbitals (one s orbital and two p orbitals) of each carbon coalesce (hybridize), that is, combine to form three identical orbitals, each called an  $sp^2$  orbital (Fig. 30.3).

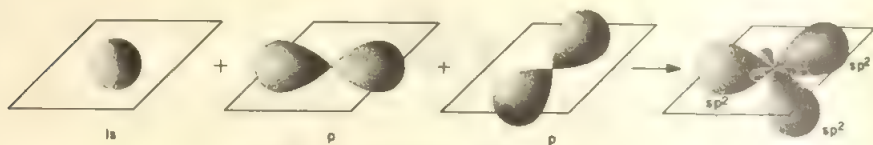
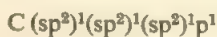


Figure 30.3.  $sp^2$  hybridization.

The three  $sp^2$  orbitals differ only in direction. They lie in the same plane and each points toward the apex of an equilateral triangle. The carbon atom becomes,



(The four valence electrons are placed, one in each orbital of the new hybridized atom.) The ethene molecule forms with sigma bonds between each pair of binding atoms, as shown in Figure 30.4.

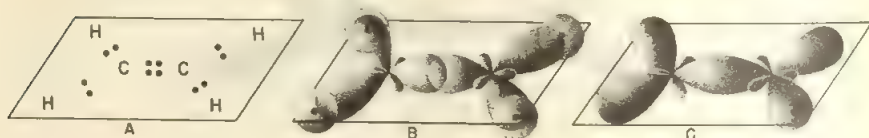


Figure 30.4. The sigma bond skeleton in ethylene.

Each atom contributes one electron for sharing in forming each bond. Five sigma (four C to H and one C to C) are formed because the occupied orbitals are symmetrical about the line between the two nuclei.

After formation of the sigma bonds there remains with each of the two carbons one p orbital perpendicular to the plane of the molecule, each with 1 electron. The p orbitals overlap as shown in Figure 30.5 to form a pi orbital in which the 2 electrons are shared. Sigma bonds are represented by straight lines.

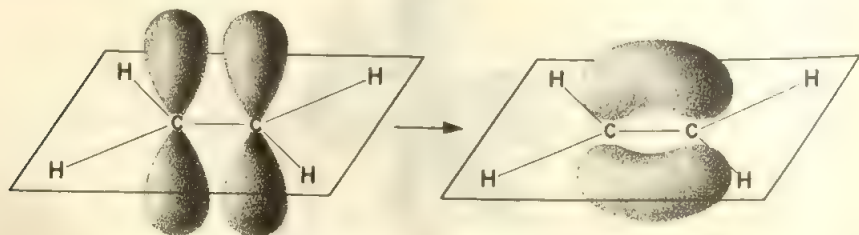


Figure 30.5. The pi bond in ethylene.



The double bond in ethylene and similar compounds is therefore of two parts, a sigma bond buried within the molecule and a pi bond in which the occupying electrons are more exposed to the influence of approaching electric fields. The orbital arrangement is not unlike a "hot dog." The frankfurter represents the sigma bond; the bun, the pi bond.

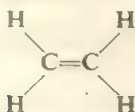
It is obvious that the double bond will differ in many respects from the single carbon to carbon bond.

(1) The carbons are held more tightly. A colliding particle requires more energy to break the molecule in half.

(2) The carbons are drawn more closely together, the distance between their centers being 1.34 Å.

(3) The bond is *rigid*. There is no rotation about the double bond. Rotation would disrupt the molecular pi orbital and destroy the bond. In ethylene all atoms maintain the same position relative to one another. Rigidity of the double bond gives rise to a type of isomerism to be discussed later.

(4) The double bond is *planar*. In more precise terms, the 2 carbons and all atoms attached to them lie in the same plane. The formula for ethylene,



places the atoms very nearly in their correct positions in the molecule.

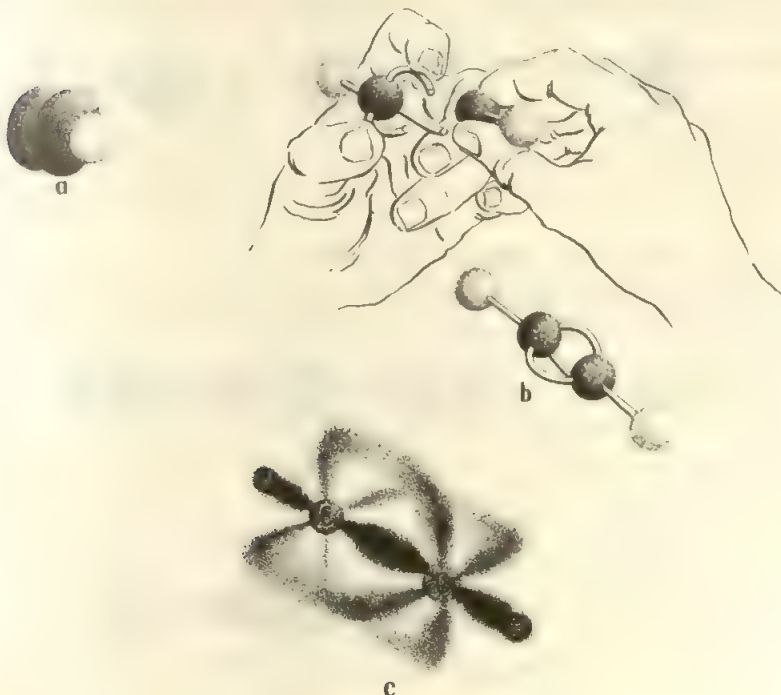
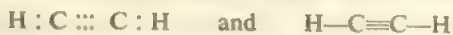


Figure 30.6. Models of acetylene.

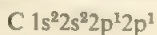
(5) Certain electrons (pi electrons) are more exposed than electrons of the single C—C bonds.

### B. THE TRIPLE BOND

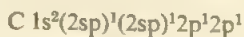
Acetylene ( $C_2H_2$ ) contains a triple bond. Structural formulas are:



The sharing of 6 electrons by the carbons is necessary if the carbons are to have the noble gas configuration. Figure 30.6 contains three representations of the acetylene molecule. The relative sizes and positions of the atoms are shown in Figure 30.6a. Figure 30.6b illustrates the bonding that would result if three of the bonds from each carbon were bent together from their tetrahedral angles. The modern molecular orbitals are shown in Figure 30.6c. Again the C—H bond is not altered although the triple bond leads to a linear structure for acetylene and related molecules. The C to C triple bond may be considered to be a bond of three parts. Each carbon atom of ethyne (acetylene) which originally had the electron structure



with four valence electrons, is hybridized upon formation of the triple bond to



That is, the 2s orbital and a p orbital combine to give two sp orbitals (Figure 30.7).

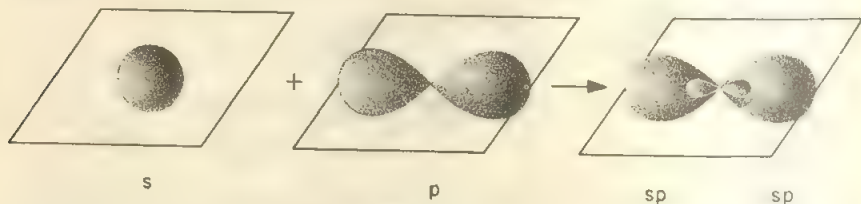


Figure 30.7.

One sp orbital forms a sigma bond with a hydrogen atom and the other with the neighboring carbon atom (Fig. 30.8).

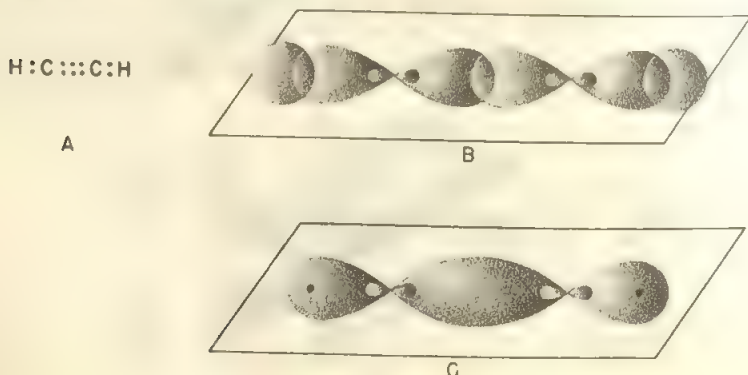


Figure 30.8.

In addition there remain with each carbon two electrons, each in a p orbital—the p orbitals being perpendicular to one another and perpendicular to the sigma bond between them. Each pair of p orbitals overlaps to form pi bonds (Fig. 30.9). This configuration corresponds to a hypothetical hot dog with two buns. The frankfurter is the sigma orbital and each of the buns is a pi orbital.

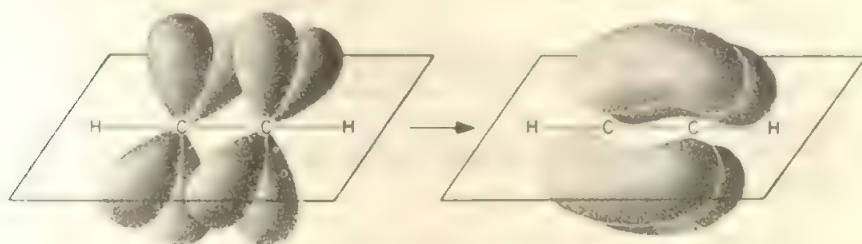


Figure 30.9.

Compared to the single and double bonds:

- (1) The triple bond is a stronger bond.
- (2) The two carbon atoms are held more closely, the bond distance being 1.21 Å.
- (3) The bond is *rigid*; there is no rotation, but this is of no consequence, because the single bond extending from the triple bonded carbon permits rotation.
- (4) The triple bond is *linear*. That is, the carbons and atoms attached to them lie in a straight line.
- (5) Certain electrons, the pi electrons, are more exposed than electrons of the single C to C bond. There are more of these exposed electrons in the triple bond than in the double bond (4 as compared to 2), but the degree of exposure is much the same.

### 3. NOMENCLATURE

Any open chain carbon-hydrogen compound which contains, in addition to single carbon to carbon bonds, only one double C to C bond is called an *alkene*. Hydrocarbons with two double bonds are called *alkadienes*; with three, *alkatrienes*, etc. A cyclohydrocarbon with one double bond is a *cycloalkene*. Any open chain hydrocarbon which contains, in addition to single C to C bonds, only one triple C to C bond is called an *alkyne*. Compounds containing more triple bonds are called *alkadiynes*, *alkatriynes*, etc. A compound containing both a double C to C bond and a triple C to C bond is correctly called an *alkenyne*. In this text it is sufficient to give the common names for a few of the compounds, the IUPAC nomenclature system for the alkenes and alkynes, and the systematic names for a few more complicated hydrocarbons.

Several alkenes and one alkyne are well known and carry common names. These are shown with structural formulas in Table 30.1.

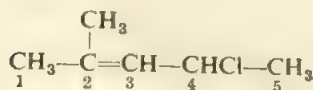
The IUPAC rules for naming alkenes and alkynes are necessary extensions and adjustments of the rules for naming alkanes.

- (1) Select the longest continuous chain *containing the multiple bond*.
- (2) Name the chain as though it were an alkane, but change the ending to *ene* if the multiple bond is a double bond, or to *yne* if the multiple bond is a triple bond.
- (3) Number the carbons of the chain beginning at the end nearest the multiple bond.
- (4) Indicate the position of the multiple bond (if necessary) by placing the number of the first carbon to which the double bond is attached immediately preceding the stem name.
- (5) Complete the name, naming and indicating the position of groups as with alkanes.

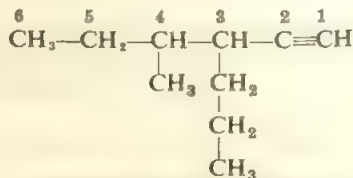
**Table 30.1. Names and Structural Formulas of Some Alkenes and Alkynes**

<i>Formula</i>	<i>Common Name</i>	<i>IUPAC Name</i>
$\text{CH}_2=\text{CH}_2$	ethylene	ethene
$\text{CH}_3-\text{CH}=\text{CH}_2$	propylene	propene
$\text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}_2$	$\alpha$ -butylene	1-butene
$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3$	$\beta$ -butylene	2-butene
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3-\text{C}=\text{CH}_2 \\   \\ \text{CH}_2-\text{CH}_2 \\ / \quad \backslash \\ \text{CH}_2 \quad \text{CH}_2 \\ \backslash \quad / \\ \text{CH}=\text{CH} \\   \\ \text{HC}\equiv\text{CH} \\   \\ \text{CH}_3-\text{C}\equiv\text{CH} \end{array}$	isobutylene	2-methylpropene
$\begin{array}{c} \text{CH}_2 \quad \text{CH}_2 \\ / \quad \backslash \\ \text{CH}_2 \quad \text{CH}_2 \\ \backslash \quad / \\ \text{CH}=\text{CH} \end{array}$	—	cyclohexene
$\text{HC}\equiv\text{CH}$	acetylene	ethyne
$\text{CH}_3-\text{C}\equiv\text{CH}$	—	propyne

A few simple applications of the naming system are found in Table 30.1. A few more examples are



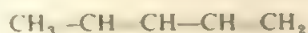
4-Chloro-2-methyl-2-pentene



4-Methyl-3-n-propyl-1-hexyne



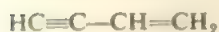
Note the names of a few hydrocarbons with 2 or more multiple bonds.



1,3-Pentadiene



2-Methyl-1,3-butadiene



3-Butene-1-yne

#### 4. PHYSICAL PROPERTIES

The physical properties of hydrocarbons with double and triple bonds are very similar to the properties of alkanes with the same number of carbons (Table 30.2).

**Table 30.2. Physical Properties of Some Hydrocarbons with Multiple Bonds**

Name	Melting Point °C	Boiling Point °C	Density (Liquid)
Ethene	-169.4	-102.4	0.610
Propene	-185	-47.7	0.610
1-Butene	-130	-6.5	0.626
1-Pentene	-138	30.1	0.642
1-Hexene	-98.5	63.5	0.675
Ethyne	-81.6	-83.6	0.621
Propyne	-104.7	-23.3	0.678
1,3-Butadiene	-108.9	-3	0.650
Cyclopentene	-93.3	44.2	0.772

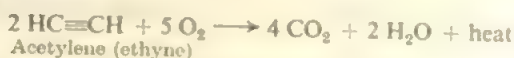
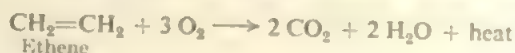
Like the alkanes, those with 4 or fewer carbons per molecule are gases. Those with 5 or more carbons are liquids. All are less dense than water. Hydrocarbons with double and triple bonds are more soluble in water, because the positive hydrogens of water are attracted slightly to the exposed pi electrons. Even so, the solubility is very slight.

#### 5. CHEMICAL PROPERTIES

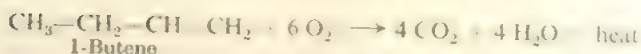
##### A. COMBUSTION

All reactions of the alkanes are available to hydrocarbons containing multiple bonds because all but the smallest members have alkane portions. All have carbon to hydrogen bonds. Except for combustion, alkane reactions

are eclipsed by faster multiple bond reactions with the same reagents. As with alkanes, combustion occurs only with ignition. Some examples are



and



The acetylene torch mixes acetylene and pure oxygen gas, which burn at a temperature sufficiently high to melt steel.

### B. ADDITION REACTIONS

Many chemicals add very readily to multiple carbon to carbon bonds. Hydrogen bromide is one such reagent. Typical reactions which occur when a hydrocarbon gas is bubbled into concentrated hydrobromic acid solution are as follows:

- (1)  $\text{CH}_2=\text{CH}_2 + \text{HBr} \longrightarrow \text{CH}_3\text{CH}_2\text{Br}$   
Concentrated
- (2)  $\text{CH}_3\text{CH}=\text{CH}_2 + \text{HBr} \longrightarrow \text{CH}_3\text{CHBrCH}_3$
- (3)  $\text{CH}\equiv\text{CH} + \text{HBr} \longrightarrow \text{CH}_2=\text{CHBr}$
- (4)  $\text{CH}_2=\text{CHBr} + \text{HBr} \longrightarrow \text{CH}_3\text{CHBr}_2$

Each double bond can add only one molecule of HBr as shown in reactions (1) and (2). The triple bond, however, has double the ethylene capacity for adding HBr. Acetylene, as shown in reactions (3) and (4), adds either one or two molecules depending upon the amount of HBr provided and the reaction conditions used. Equations do not show the mechanism of the reaction, but they do show the initial and final compounds. Thus, one should realize that reactions (2) and (3) might form other by-products, as they do. Each equation gives only the principal product. From the equations one can see that the reaction is an *addition* reaction. The reagent HBr was added, not substituted. The ready addition of this and other reagents to multiple bonds has earned the name *unsaturated* for the compounds possessing them. Alkanes and substituted alkanes, compounds containing only single bonds, are termed *saturated*.

Consideration of the mechanisms (intermediate steps) in the four reactions with hydrogen bromide reveals the reason for the great activity of multiple bonds with addition reagents. It should help one to choose the principal product when more than one is possible.

**(1) Reaction of Ethene with Concentrated Hydrobromic Acid.** The partly exposed pi electrons of the ethene (ethylene) molecule gives the double bond a negative character. Positive ions, or the positive ends of polar mole-

cules are attracted to the double bond. The approaching positive charge attracts the pi electrons and distorts the pi bond (Fig. 30.10).

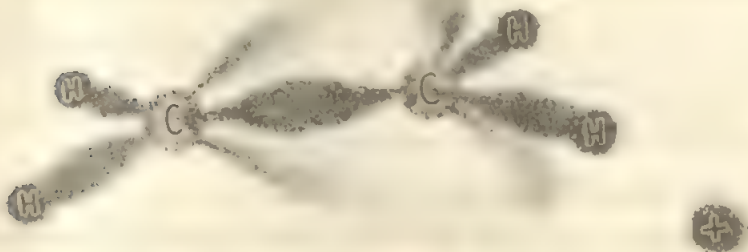
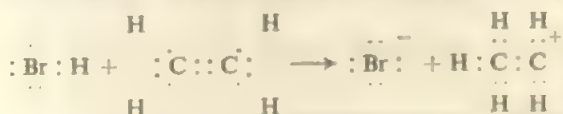
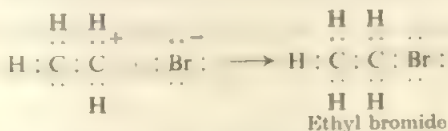


Figure 30.10. Effect of a positive charge on the pi bond.

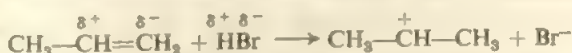
In the reaction under discussion, the hydrogen of the hydrogen bromide molecule carries the approaching positive charge. The pi electrons are drawn toward the hydrogen and bond with it, releasing the bromide ion.



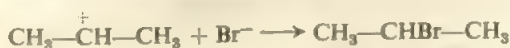
The negative bromide ion or a bromide ion from another HBr molecule then combines with the  $\text{CH}_3\text{CH}_2^+$  ion.



(2) **Reaction of HBr with Propene.** The hydrogen bromide molecule approaches the pi orbital with the positive H drawn toward the pi electrons. But the *terminal* (end) carbon of the double bond is the more negative of the two. The hydrogen of the HBr molecule draws the pi electrons and is attached preferentially at that point:



The bromide ion then combines at the positive center carbon:

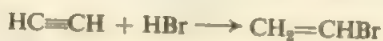


This agrees with a rule formulated by a Russian scientist, V. Markownikoff, which may be stated in these terms. "When an *unsymmetrical* reagent adds to an *unsymmetrical* multiple bond, the positive part of the adding reagent

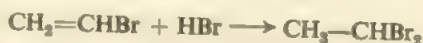
goes to the carbon of the double bond to which the greater number of hydrogen atoms is attached." Hydrogen bromide is *unsymmetrical*; H is different from Br (and more positive). Propene is *unsymmetrical*.  $\text{CH}_3\text{CH}=\text{CH}_2$  differs from  $\text{CH}_2=\text{CHCH}_3$ .

The more positive part of the reagent (H) adds to the carbon with the more hydrogens ( $=\text{CH}_2$ ). The product formed in larger amount is 2-bromopropane, as written, and not 1-bromopropane, which would have resulted had the HBr added oppositely.

(3) **Reaction of HBr with Acetylene.** Addition of the first molecule of hydrogen bromide can yield only one product:



By Markownikoff's rule the (H) of the next molecule of HBr must add to the  $\text{CH}_2=$  and not to  $\text{CHBr}=:$

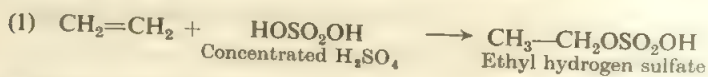


The product is 1,1-dibromoethane and not 1,2-dibromoethane.

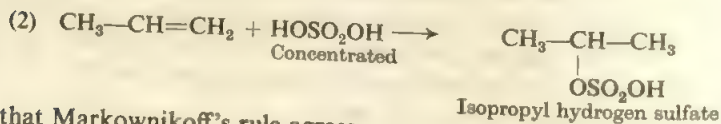
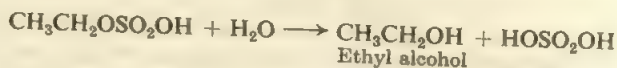
(4) **Other Addition Reactions.** Two other hydrogen halides, HI and HCl, add to multiple C to C bonds from concentrated solutions. The mode of *addition* is similar to that of HBr. Other addition reagents with optimum conditions of reaction, and equations for typical reactions are listed below:

(a) *Hydrohalic acids.* HCl, HBr and HI from concentrated solutions (discussed above).

(b) *Hydrogen sulfate* from concentrated sulfuric acid:

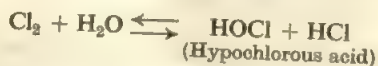


This reaction is an intermediate step in an industrial preparation of alcohols, ethyl alcohol in this case. With water, ethyl hydrogen sulfate is converted to an alcohol:



Note that Markownikoff's rule agrees.

(c) *Hypohalous acid.*  $\text{HOCl}$  adds to a multiple bond. As discussed in Chapter 15, the halogens are only slightly soluble in water. However, part of the halogen is found in the form of the hypohalous acid by the reaction illustrated here using chlorine as an example.



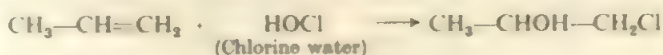
Of the substances present in a halogen solution (the halogen, water, the



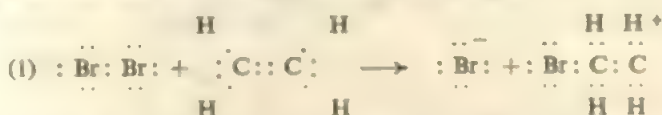
hydrohalic acid and the hypohalous acid) the hypohalous acid is the most reactive addition reagent. With chlorine water this reaction occurs with multiple bonds:



Of the two addition fragments HO and Cl, chlorine is more positive. In agreement with Markownikoff's rule the reaction with propene is:

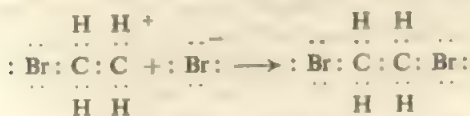


(d) The halogens bromine and chlorine add rapidly to multiple bonds. The reaction with ethene is believed to occur in these steps:

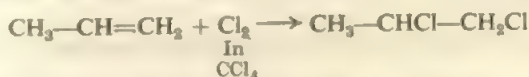


At the moment of collision, bromine adds as a positive bromine ion with 6 electrons utilizing the 2 pi electrons to form a bond and the positive  $\text{BrCH}_2-\text{CH}_2^+$  ion:

(2) The positive ion reacts with the bromide ion:

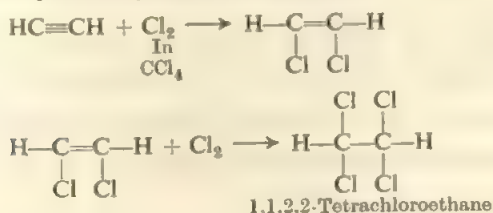


One evidence for this mechanism is the fact that when sodium chloride is added to the bromine solution, some 1-bromo-2-chloroethane is formed. With propene the reaction is:



Water cannot be used as the solvent, for the hypohalous acid would be formed and would add. Carbon tetrachloride or some other inert non-polar solvent is used. Notice that the halogen is a *symmetrical* addition reagent. Only one addition product is possible.

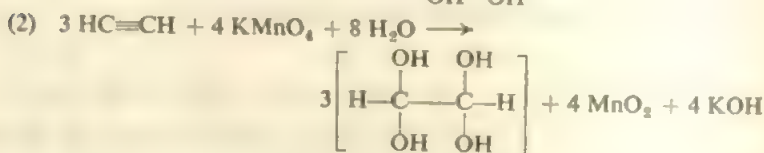
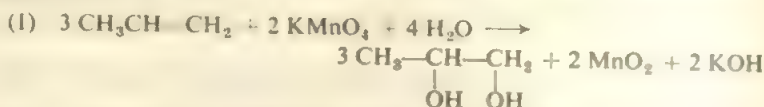
With ethyne (acetylene) the reaction is:



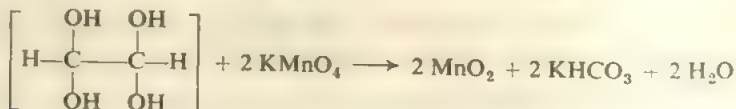
A convenient *laboratory test* for multiple bond (unsaturated) compounds is made by shaking the hydrocarbon with a bromine solution in carbon tetra-

chloride. If multiple bonds are present, the reddish-brown solution is decolorized as colorless bromo alkanes form and dissolve in the carbon tetrachloride. An alkane will decolorize a bromine-tetrachloride solution in sunlight, but the substitution reaction is slow and hydrogen bromide fumes appear.

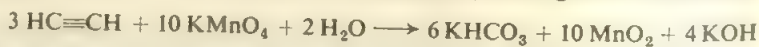
(e) *Unsaturated hydrocarbons are oxidized rapidly by solutions of potassium permanganate and other strong oxidizing agents.* The reaction is listed here, because in the reaction hydroxyl groups ( $\text{—OH}$ ) are added to the carbons of the multiple bond.



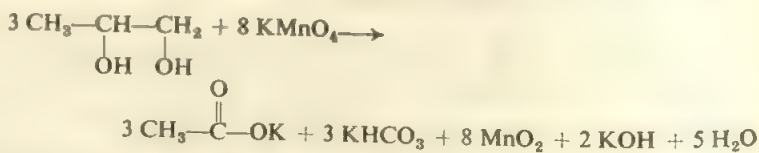
It is difficult to arrest the oxidation of an alkene at the dihydroxy stage. However, if a *dilute*, neutral solution of permanganate is used at low temperature, it is sometimes possible. It is impossible to stop the alkyne oxidation at the tetrahydroxy stage. Hence the brackets about the compound. The brackets indicate a *transient species*, one that is not isolated but is thought to occur in the course of the reaction. The reaction proceeds further to break the C to C bond:



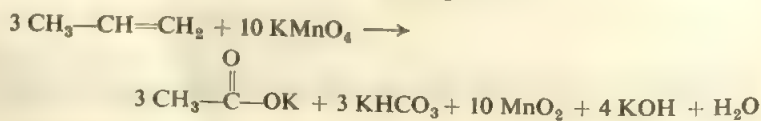
The complete reaction of acetylene with potassium permanganate solution is:



When either acidic or basic solutions of potassium permanganate are used or when the temperature is raised, the dihydroxy compound formed in the first stage of oxidation of an alkene is oxidized further. With propene reaction (1) is followed by:

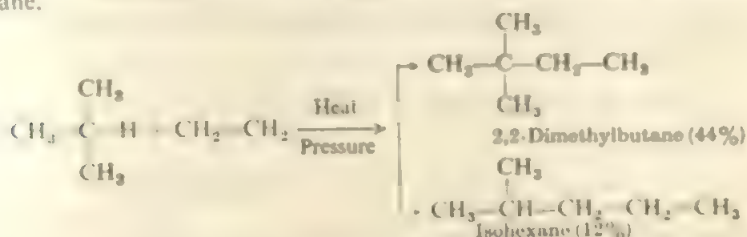


The equation for the complete oxidation of propene is:



These reactions are the bases for the *Baeyer's test* for unsaturation (multiple bonds). A potassium permanganate solution is purple. Manganese dioxide is a dark brown precipitate. If a solution of potassium permanganate is decolorized when shaken with a hydrocarbon and a brown precipitate appears, the test is positive, the compound is unsaturated.

(f) *Alkylation*. A saturated hydrocarbon may add to a multiple bond. Addition may take place either at high temperature and high pressure or at moderate temperature and pressure with suitable catalysts. Isobutane adds to ethylene at 510° and 300 atmospheres to form isohexane and 2,2-dimethylbutane.

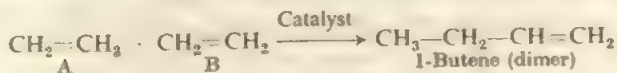


The formulas of the major products correspond to a cleavage of the alkane into a hydrogen and an alkyl group, which add to the double bond.

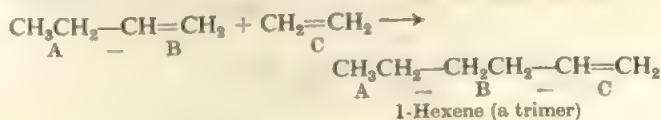
Alkylation with one of the catalysts, aluminum chloride, sulfuric acid, or liquid hydrogen fluoride, may be carried out at temperatures between  $-30^\circ\text{C}$  and  $100^\circ\text{C}$  and at pressures from 1 to 5 atmospheres, depending on the compounds. Apparently an entirely different course of reaction is followed from that of the thermal reaction. A complex mixture of branched alkanes is obtained. The mechanism of the reaction appears to be very complicated. Nevertheless the reaction is most important as it produces highly branched alkanes for high octane fuels.

(g) *Polymerization occurs among compounds with multiple bonds. Polymerization is merely self-addition. Polymers are compounds of high molecular weight formed by the joining together of many small similar or identical units. The small unit is called a monomer.*

The self-addition of ethylene (ethene) is an excellent example. One molecule of ethylene (B) may add to another (A) to give 1-butene.



1-butene is made of 2 monomer molecules and is therefore a dimer. But 1-butene has a double bond to which a third molecule of ethylene (C) may add.

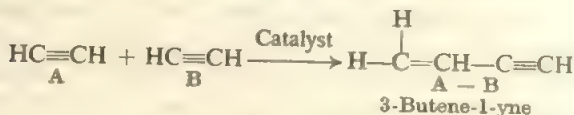


Self-addition may continue indefinitely to give a polymer of many units. The

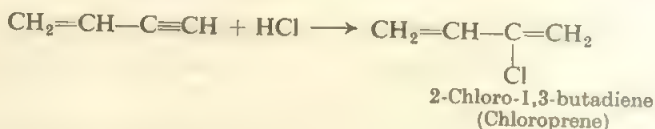
product is polyethylene, the tough flexible plastic used for making cups, refrigerator dishes, etc.

The conversion of acetylene to neoprene rubber, which is very similar in structure to natural rubber, is a good example of polymerization.

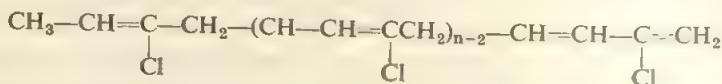
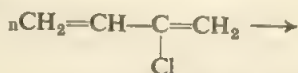
The first step in the process is the catalytic dimerization of acetylene:



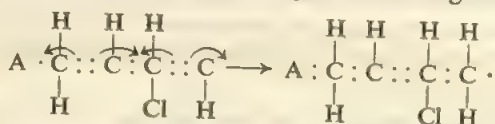
The controlled addition of HCl from concentrated hydrochloric acid gives a substituted alkadiene:



Polymerization of chloroprene yields the long chain molecules of isoprene rubber:

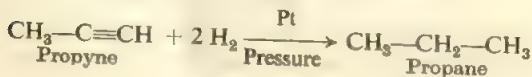
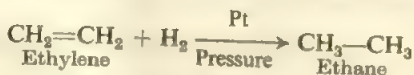


$n$  is the number of chloroprene units in the polymer. It is a large number. All units in the molecule except the end units are identical. The addition in the last step is a little different from that discussed above. An atom, or some other group (A), with 1 electron joins with the first carbon, drawing 1 electron from the double bond and causing the following shift in electrons:



The  $\text{ACH}_2-\text{CH}_2=\text{CCl}-\text{CH}_2\cdot$  combines with the next chloroprene molecule as did the hydrogen; the electrons shift and a new reactive fragment is ready to add to another. The effect of the addition is the loss of one double bond by addition as usual. The difference is that the double bond that remains has been shifted to the center of the original molecule.

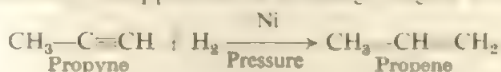
(h) *Hydrogenation*. Hydrogen gas has no observable tendency to add to a multiple bond, even at relatively high temperature in the absence of a catalyst. In the presence of finely divided platinum, palladium, nickel or iron the reaction proceeds smoothly at a few atmospheres pressure.





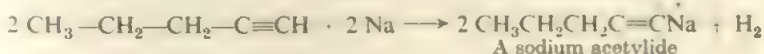
Alkanes can be prepared in this way. The method is too expensive for commercial use, because the unsaturated compound is more expensive than the alkane.

With the less active catalysts, palladium and nickel, the hydrogenation of an alkyne *can* be stopped at the first stage to give an alkene with good yield.



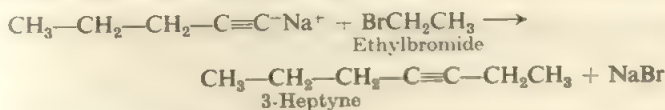
A few reactions are specific for alkynes; two should be mentioned.

(i) *The hydrogen of the end carbon of a terminal triple bond is sufficiently acidic to be replaced by sodium metal.* When sodium metal is dropped into a terminal alkyne, hydrogen is released. Bubbling occurs if the hydrocarbon is a liquid. With 1-pentyne the reaction is

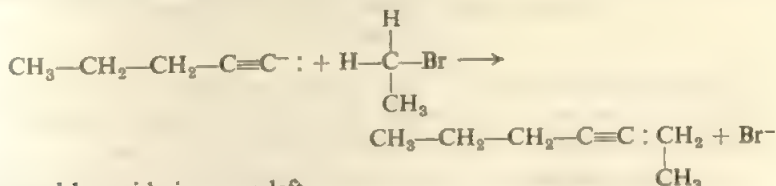


No water can be present, because the sodium will displace hydrogen from water preferentially.

Sodium acetylides can be used to prepare alkynes with longer carbon chains. The acetylide reacts with alkyl halides.



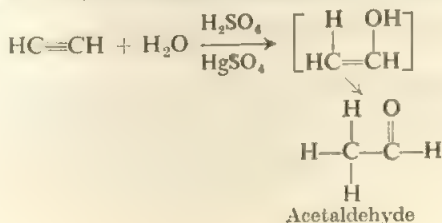
The negative acetylide ion may attack the ethyl bromide, forming a bond with the carbon which releases the bromide ion.



Sodium and bromide ions are left.

Only a *terminal* acetylene reacts with sodium. The group (HC—) must be present. Various acetylenes will react in the same manner with certain heavy metal ions (silver, mercury and copper) to give precipitates which are called acetylides. When dry, these acetylides may decompose with explosive violence.

(j) *Water will add to acetylene* in the presence of dilute sulfuric acid and mercuric sulfate to produce an unstable compound that rearranges to acetaldehyde, a very important compound to be discussed in a later chapter.



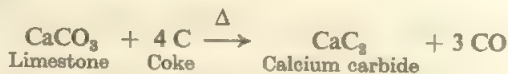
These are a few of the reactions with which a hydrocarbon is endowed by the presence of a multiple bond.

## 6. PREPARATIONS OF UNSATURATED HYDROCARBONS

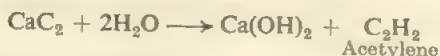
Unsaturated hydrocarbons are found (but in very small percentages) in petroleum. Ethene is often obtained when an organic substance is heated to a high temperature in the absence of air. Today, alkenes are obtained in large quantities from the "cracking" process used to obtain higher percentages of gasoline from petroleum. The smaller members, ethylene and propylene, are used extensively as raw materials for the synthetic production of many chemicals: permanent antifreeze, ethyl alcohol and acetic acid are among the most important.

Acetylene is produced from inorganic materials, as described in Chapter 28.

Calcium carbide is produced by heating limestone and coke in an electric furnace:



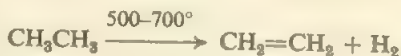
Calcium carbide is decomposed by water to yield acetylene:



### A. LABORATORY PREPARATIONS OF UNSATURATED HYDROCARBONS

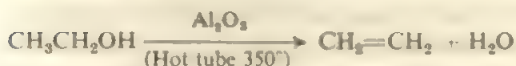
Laboratory preparations of unsaturated hydrocarbons should be called subtraction reactions, because they amount to subtracting substances from saturated compounds. They are called *elimination* reactions.

(1) **Dehydrogenation.** Alkenes may be prepared directly from alkanes in certain cases by the use of heat or under the stimulus of special catalysts such as molybdenum or chromium oxides supported on aluminum oxide. At temperatures of 500–700°C, ethane loses two hydrogen atoms, one from each carbon, to form ethylene:

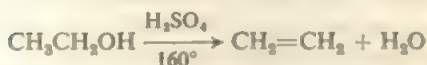
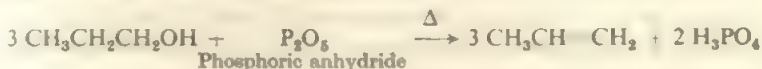


Higher alkanes form alkenes under similar conditions, but the positions in the molecule from which the hydrogen atoms will be removed cannot be predicted. A mixture of isomeric alkenes, as well as other decomposition products, is obtained.

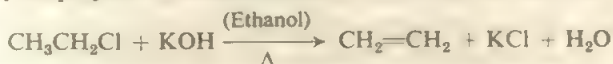
(2) **Dehydration.** Dehydration refers to the removal of the elements of water from adjoining carbons. It is an important method for preparing alkenes. Commercially, hot alcohol is passed over heated aluminum oxide ( $\text{Al}_2\text{O}_3$ ) to remove the water:



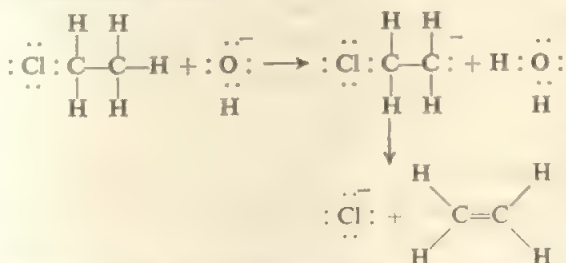
In the laboratory either phosphoric anhydride or concentrated sulfuric acid is used to remove the water:



(3) **Dehydrohalogenation.** When adjacent carbon atoms of a saturated compound have respectively one hydrogen and one halogen atom attached to them, elements of a hydrohalic acid may be removed. This elimination is called dehydrohalogenation. The transformation may be accomplished by a solution of a strong base in alcohol. Potassium hydroxide in ethyl alcohol is usually employed. The reaction may be written as follows:



The hydroxide is the attacking agent. It approaches the ethyl chloride molecule from the side opposite the halogen. A hydrogen is pulled from the carbon to form water, leaving the bonding electrons behind. The electron pair is shifted in between the carbons and the chloride ion is released. The process is illustrated below:



With the alkyl halides, the tendency toward dehydrohalogenation is greatest for tertiary halides and least for primary halides. With a given alkyl halide, the tendency toward elimination increases with increasing concentration of basic reagent; concentrated alcoholic potassium hydroxide is more effective in eliminating hydrogen halide than is an aqueous (water) solution. The hydroxide ion in water tends to replace the halide in the molecule.

## 7. PETROLEUM

Most hydrocarbons used today originate from coal, petroleum or natural gas. The latter two warrant special treatment since they are the most important natural sources of the alkanes. Natural gas is largely methane (80–85%), accompanied by progressively smaller amounts of propane, butane and the higher alkanes (3%). Petroleum, the largest source of hydrocarbons, is a

complex mixture of alkanes accompanied by varying amounts of cyclic saturated and aromatic hydrocarbons (Chapter 31), along with smaller quantities of oxygen-, sulfur- and nitrogen-containing substances.

Petroleum is a dark viscous liquid obtained from underground deposits found in the upper strata of the earth's crust. Natural gas and petroleum are trapped in the interstices of porous rocks, such as limestone or sandstone, in reservoirs capped by dome-shaped, overlying layers of nonporous rock. Drilling a well provides an outlet through this impervious cap from which natural gas and petroleum may escape or can be removed. Hydrostatic pressure of the underlying liquid present when a well is first drilled forces the natural gas and crude oil through the opening until the excess pressure is released, after which the oil is recovered by pumping.

Petroleum is separated into fractions of differing boiling range by distillation. This is called *refining*. The fractionation is accomplished in refineries located near the oil fields or in other localities to which the crude oil is moved by pipeline or other readily available transportation. Distillation of the crude oil depends on progressive separations as the boiling temperature is increased. Various fractions, the quantity and composition of which differ widely with the origin of the petroleum, are collected. The usual fractions obtained as distillate are listed in Table 30.3.

**Table 30.3. Petroleum Distillate**

<i>Fraction Name</i>	<i>Boiling Temperature, °C</i>	<i>Carbon Chain Length</i>
Gas	Below 20°	C <sub>1</sub> to C <sub>4</sub>
Petroleum ether	20–60°	C <sub>5</sub> to C <sub>6</sub>
Ligroin	60–100°	C <sub>6</sub> to C <sub>7</sub>
Gasoline	40–205°	C <sub>8</sub> to C <sub>12</sub>
Kerosene	175–235°	C <sub>12</sub> to C <sub>20</sub>
Gas oil	Above 275°	
Lubricating oil	Nonvolatile liquids	
Asphalt or petroleum coke	Residue	

Petroleum from Pennsylvania and other eastern states is composed largely of alkanes and yields paraffin as the end product of distillation. Oils of this kind are said to have a *paraffin base*. Petroleums from California, Texas and Mexico, which yield a black tarlike residue when distilled, are referred to as *asphalt base* petroleums. Midcontinent oils are a composite of both types.

Petroleum is the most important source of motor fuel, which is the chief use of the volatile fractions. Correspondingly, as the demand for gasoline has mushroomed over the years, methods have been developed for converting large quantities of the less volatile components of petroleum into smaller



molecules more useful as fuels. Simultaneously, the development of modern engines with their more exacting fuel requirements stimulated the discovery of reactions for producing fuels of greater efficiency by combining together the small molecules, usually lost during distillation of gases, into highly branched hydrocarbons having boiling points within the gasoline range.

The quality of gasoline as a fuel is expressed by its *octane number*. This is a figure obtained by comparing the performance of a standard one cylinder test engine when using the gasoline concerned as a fuel with the performance of this same test engine when operated using a blend of two synthetic fuels, isooctane (2,2,4-trimethylpentane) and n-heptane. Isooctane is assigned an octane rating of 100, n-heptane a rating of 0. The octane number is the per cent of the octane present in a fuel mixture with n-heptane which exhibits the same knocking characteristics as the gasoline being examined. Knock refers to the ping that occurs when an automobile engine is accelerated too rapidly. The existence of a knock, or ping, is an indication that conditions for efficient performance of the engine with the fuel being used has been exceeded. A gasoline whose performance corresponds to that of a mixture containing 90% isooctane and 10% heptane would have an octane number of 90.

Numerous substances are known to increase the octane ratings of fuels. Highly branched alkanes, unsaturated hydrocarbons (alkenes) and aromatic hydrocarbons, when present, materially improve the antiknock quality of gasoline. Manufacturing procedures which increase the percentage of molecules of these types in gasolines are widely used. *Cracking*, or *pyrolysis*, (Chapter 29) accomplishes the cleavage of large alkanes (nonvolatile components) into smaller molecules. Cracking carried out in the presence of catalysts which speed up the reactions taking place is known as *catalytic cracking*. Almost all refineries have at least one catalytic cracker. The pyrolysis yields a mixture of alkanes and alkenes. The process, therefore, increases the quantity of gasoline obtained from a given petroleum, while simultaneously giving a superior product because of the increased percentage of alkenes present. Gasoline made by cracking requires protection to prevent oxidation, which initiates polymerization and leads to gum formation. Antioxidants of various types are added to some gasolines to prevent this type of deterioration.

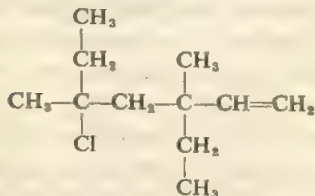
*Alkylation*, discussed earlier in this chapter, refers to the addition of branched alkanes to alkenes under atmospheric pressure at a relatively low temperature in the presence of a suitable catalyst. The reaction provides a direct route to highly branched alkanes, *giving fuels of improved anti-knock characteristics*, and avoids the necessity for hydrogenation or the use of antioxidants. *Isomerization* (Chapter 29) also increases the percentage of highly branched isomers in a given hydrocarbon mixture. Again a fuel of superior quality is obtained.

*Aromatization*, or *reforming*, refers to the catalytic process used to convert cyclohexanes, cyclopentanes and alkanes into aromatic hydrocarbons (Chapter 31). Since most aromatic hydrocarbons suitable as fuels exhibit octane numbers above 100, a product of markedly improved antiknock quality is obtained.

Other substances not formed from petroleum itself which might be added to gasoline to improve its antiknock properties are also known. Of these, the metal alkyls are the most effective. The best known of these is tetraethyllead,  $(C_2H_5)_4Pb$ , which is added to the gasoline, together with ethylene bromide and ethylene chloride. The latter two compounds prevent deposition of lead oxide in the engine since they convert the lead oxide formed into volatile lead halides. About 95% of all American gasolines contain added tetraethyllead and are known as *ethyl gasolines*.

### EXERCISES

- Write the electron dot formula (valence electron structure) for (a) ethylene, (b) propylene and (c) acetylene.
- Define functional group.
- Write both the common names and the IUPAC names for each alkene containing no more than 4 carbons.
- Write structural formulas for and name each of the isomeric pentenes by the IUPAC system.
- Compare the C to C bonds in ethane, ethylene and acetylene in regard to length, rigidity and chemical reactivity.
- Write structures for and name all possible compounds with the formula  $C_4H_8$ .
- Name this compound:



- Define substitution reaction and addition reaction. Which is characteristic of alkenes?
- Write equations for the reaction of propene with (a) concentrated HCl, (b) chlorine water, (c) chlorine gas and (d) hydrogen gas. Show special conditions and catalysts, if any.
- (a) Define "unsymmetrical double bond." Illustrate.  
(b) Define "unsymmetrical addition reagent." Illustrate.
- State Markownikoff's Rule. Illustrate its application.
- Write equations for a 2 step preparation of  $CH_3CHOHCH_3$  (isopropyl alcohol) from propene.
- Define dimer, trimer, polymer and polymerization.
- Write structural formulas for and name all acetylenes having from 2 to 5 carbons.
- Write equations for the stepwise addition of the following reagents to acetylene (show catalysts and special conditions on the arrow): concentrated HBr, hydrogen gas.
- Write equations for 2 reactions of 1-butyne that are impossible for any of its isomers.
- Write equations for the preparation of:
  - propene from 2-bromopropane
  - propene from 1-propanol ( $CH_3CH_2CH_2OH$ )
  - propyne from propene (2 steps)
  - ethane from 1-butene (2 steps)
  - propene from propane (2 steps)
  - cyclohexene from bromocyclohexane.



## AROMATIC HYDROCARBONS

Benzene is a familiar and widely used industrial chemical obtained as a volatile by-product during the production of coke from coal. It is the simplest of a class of organic substances known as aromatic compounds; the term aromatic refers to the characteristic fragrance of some of the first compounds of this class to be discovered. The odor however has no significance today in defining the chemical nature of such substances.

### 1. THE BENZENE MOLECULE

Benzene, discovered in 1825 by Michael Faraday, is a hydrocarbon. Repeated analyses and a molecular weight determinations show it to have the formula  $C_6H_6$ , which, as such a formula would ordinarily be interpreted, implies that it is a highly unsaturated compound. However, such is not the case. Chemically its behavior differs markedly from that of alkenes or alkynes. It does not exhibit the familiar reactions of unsaturated hydrocarbons. It does not give a positive Baeyer's test, nor does it readily decolorize bromine water, both of which are tests for the presence of unsaturation. The more usual action of reagents on benzene and related compounds is to replace or substitute one or more of its hydrogen atoms. Nitric acid reacts to give nitro-substituted derivatives. Sulfuric acid substitutes an  $-SO_3H$  group for a hydrogen atom.

This unique chemical behavior of a supposedly unsaturated hydrocarbon, benzene, is referred to as *aromatic character*, and compounds of similar behavior are said to exhibit *aromaticity*.

The search for a satisfactory structural formula for benzene is a classical example of the study often required before a consistent structural formula can be assigned to a compound. The problem began with the discovery of

benzene and has continued almost to the present day. The earliest reasonable structure proposed for benzene was that offered by Kekulé in 1865. Kekulé represented the benzene molecule as a ring of six carbon atoms joined by alternate single and double bonds (Fig. 31.1).

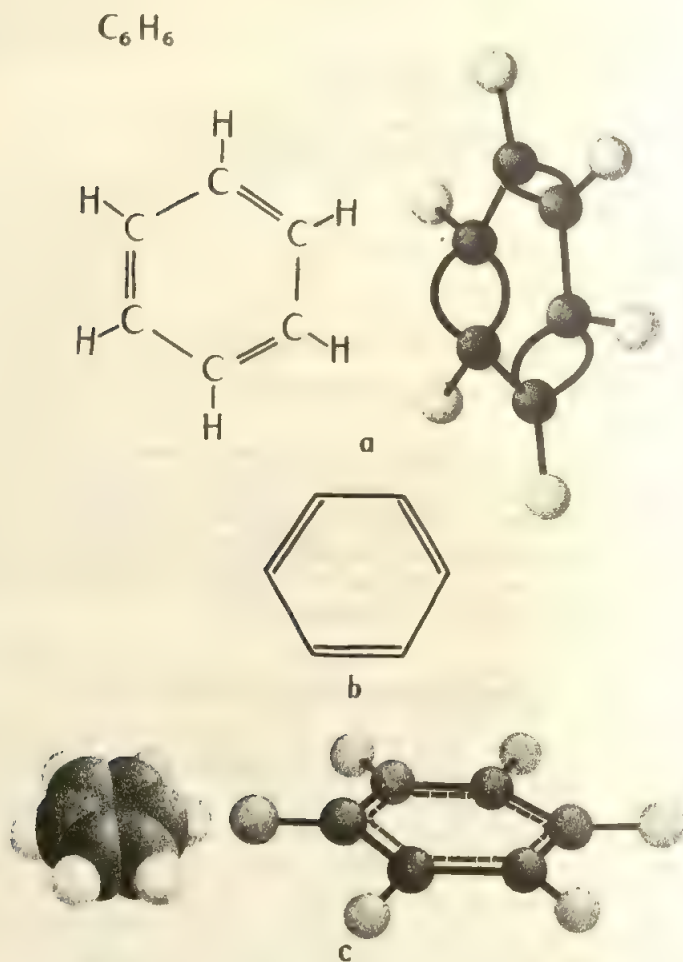


Figure 31.1. Proposed structures of the benzene molecule.

From the brief resumé of the chemical nature of benzene given in an earlier paragraph, it may be seen that this structure is not entirely suitable because of its implication that benzene has certain chemical characteristics, such as unsaturation, which the compound does not exhibit. Although this notation (Fig. 31.1a,b) is still widely used today, the meaning which it conveys for modern organic chemists is quite different from that intended by Kekulé.

One of the most useful structural formulations is that based upon the theory



of resonance, a theory proposed in the early 1930's and whose development has continued to the present. According to this theoretical picture the double and single bonds do not exist as such in the six-membered carbon ring. The single and double bonds of the Kekulé formulation have coalesced into a new kind of bond, a type having characteristics intermediate between those of a single and of a double bond. The actual structure of benzene, on this basis, is a planar six-membered ring of carbon atoms joined by six equivalent bonds of this new type. Attached to each carbon is one hydrogen atom lying outside, but in, the plane of the ring (Fig. 31.1a). Since all bonds joining the carbon atoms are alike, the molecule is a regular hexagon and is symmetrical.

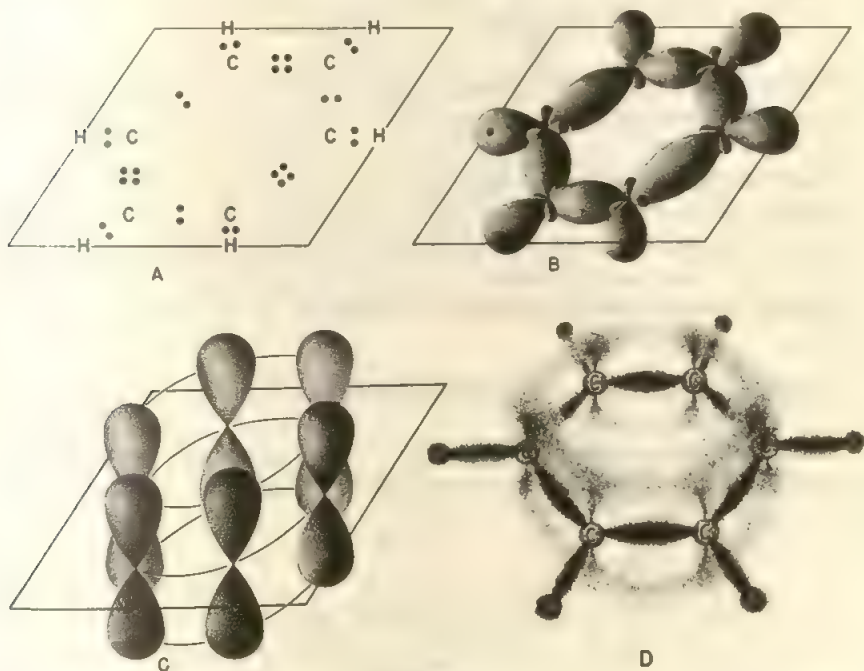


Figure 31.2. Molecular orbital representation of benzene. For further explanation, see text.

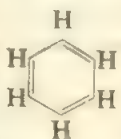

All carbons occupy identical positions, and all hydrogens are exactly alike.

Modern molecular orbital method calculations indicate that benzene is composed of six carbon atoms, each at a corner of a regular hexagon. The orbitals of each carbon are hybridized to give the  $sp^2$  configuration of carbon as found in ethylene. Each carbon atom is attached through sigma bonds to a hydrogen atom outside but in the plane of the ring and to the two neighboring carbons (Fig. 31.2b).

Each carbon atom has an unpaired electron and a p orbital perpendicular to the plane of the ring. These overlap to form pi orbitals above and below the ring. Orbitals that involve all six carbon centers are shown in Figure 31.2c. These 6 electrons occupy  $\pi$ -like orbitals above and below the ring,

similar to two doughnuts. The 6 electrons are not restricted to orbits between or about 2 atoms, but the orbits are delocalized. All 6 occupy the "double doughnut" orbitals (Fig. 31.2d). The exposed but lightly populated  $\pi$  orbitals give special properties to the aromatic bond. Actual measurements of the molecule by electron diffraction reveal only one kind of carbon to carbon bond in benzene, a bond with a length of 1.39 Å, a distance intermediate between the single bond (1.54 Å) and the double bond (1.34 Å).

Because there is no quick way to represent the benzene molecule as it really

is, the Kekulé notation  or merely  will be used throughout

the remainder of the text to represent benzene and related compounds. The student must remember the real structure, despite necessarily inadequate symbols.

There are aromatic-like substances other than benzene; several will be identified in the following section dealing with nomenclature. These often have two or more benzene type rings, with two rings sharing a bond between them. The Kekulé notation shows alternate double and single bonds. Again, one must remember that in benzene all the bonds are equivalent aromatic bonds.

## 2. NOMENCLATURE

Many aromatic compounds have long had names which have been adopted as official IUPAC names. A few are represented and named in Figure 31.3.

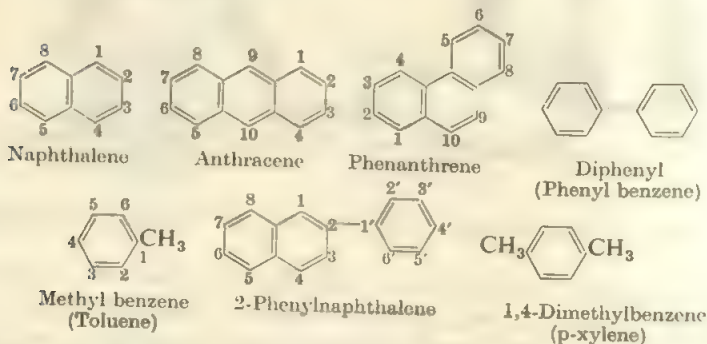


Figure 31.3. Some common aromatic compounds.

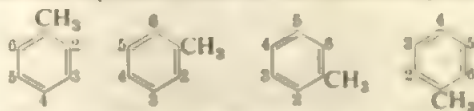
Incidentally, one should know from its formula as represented that the molecular formula for anthracene is  $C_{14}H_{10}$ .

Other aromatic compounds are named as derivatives of these. Branches on the rings are named in alphabetical order and numbered as with open chain hydrocarbons. The number is the number of the carbon in the ring to which

they are attached. The accepted pattern for numbering the rings in aromatic compounds is illustrated in Figure 31.3. Often, though not always, the numbering is done in a clockwise fashion about the complete ring system.

In naming a benzene derivative (a benzene ring with branches) the carbons are numbered from 1 to 6, beginning with one to which a substituent is attached and continuing in a direction to give the smallest numbers to the name. For example, the methyl group of toluene (methyl benzene) is always on carbon number 1.

Obviously these are representations of the same compound:



All positions are equivalent. In each there is a methyl group on the *first* carbon:

This compound or is 1,2-dichlorobenzene. The “principle of lowest numbers” is obeyed.

This compound is named 2-chloro-1,4-dimethyl benzene. No other number system will give such small numbers. More compounds are named in Figure 31.4.

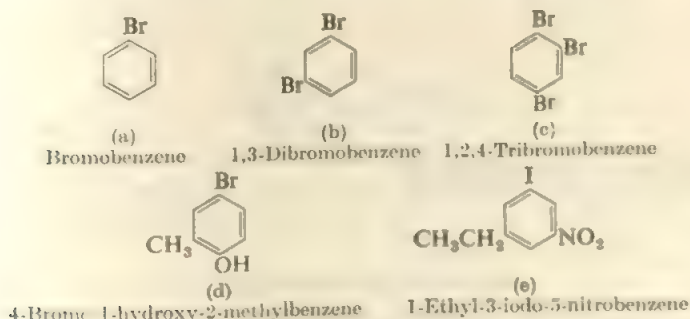


Figure 31.4. Names of some benzene derivatives.

Only two substituents be attached to the ring to give a disubstituted derivative. The prefixes *ortho*, *meta* and *para* may be used to designate the location of the two attached atoms or groups, providing no ambiguity results (Fig. 31.5).

Thus when two substituents are on adjacent (1,2) carbons (Fig. 31.5a,d) the compound is designated as the *ortho* isomer; if two substituents are on alternate (1,3) carbons (Fig. 31.5b) it will be a *meta* isomer; and if the substituents are on opposite (1,4) carbons directly across the ring (Fig. 31.5c), the compound is referred to as a *para* isomer.

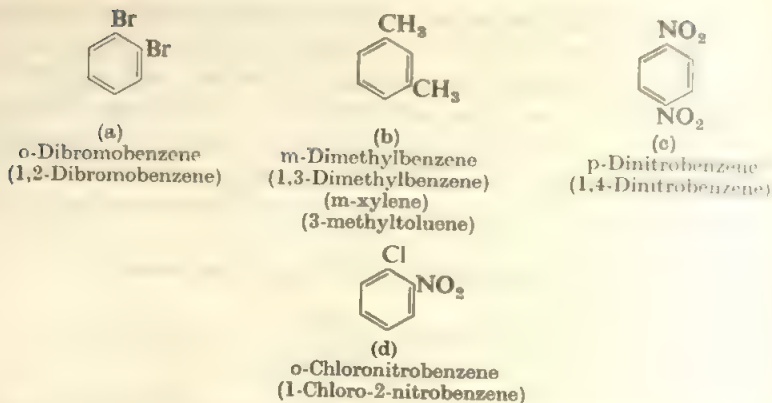
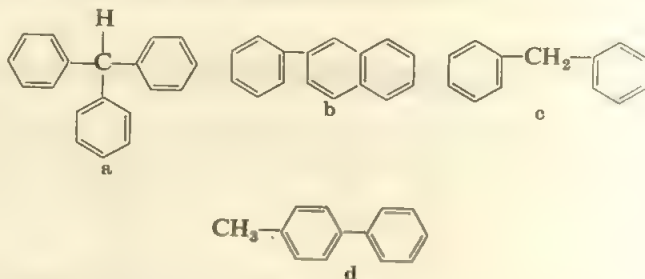


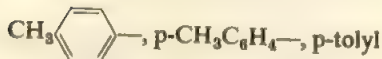
Figure 31.5. Names of some disubstituted benzenes.

Other compounds derived from benzene may be named as substitution products of commonly known benzene derivatives, such as toluene or the xylenes (Fig. 31.3). For example, 2-ethyl-1-methylbenzene may be correctly named as o-ethyltoluene or 2-ethyltoluene.

At times one finds it necessary to name an aromatic portion of a molecule as a branch. These compounds exist.



Names of some of the groups are:



Compound a is triphenyl methane

Compound b is 2-phenylnaphthalene

Compound c is diphenylmethane or benzylbenzene


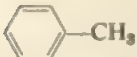
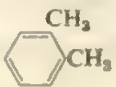
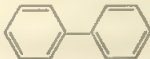
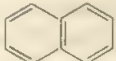
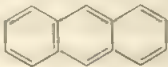
Compound d is 1-methyl-4-phenylbenzene or p-tolylbenzene



## 3. PHYSICAL PROPERTIES OF AROMATIC HYDROCARBONS

Individual aromatic hydrocarbons have physical properties very near those of other hydrocarbons containing the same number of carbons. Since the smallest aromatic compound, benzene, has six carbons, it follows that none are gases at room temperature, but are liquids up to 10 or 12 carbons. The compact benzene ring increases the density. Hydrocarbons with only one

Table 31.1. Physical Properties of Aromatic Compounds

<i>Name</i>	<i>Formula</i>	<i>Melting Point, °C</i>	<i>Boiling Point, °C</i>	<i>Density</i>
Benzene		5.51	80.1	0.879
Toluene		-95	110.6	0.867
o-Xylene		-29	144.4	0.880
Diphenyl		70	254	1.180
Naphthalene		80.2	217	1.145
Anthracene		217	354	1.25

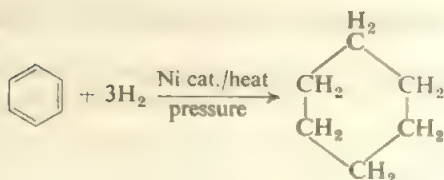
benzene ring are less dense than water. Those with more rings are more dense. All are insoluble in water. Table 31.1 gives the physical properties of some aromatic compounds.

## 4. CHEMICAL PROPERTIES

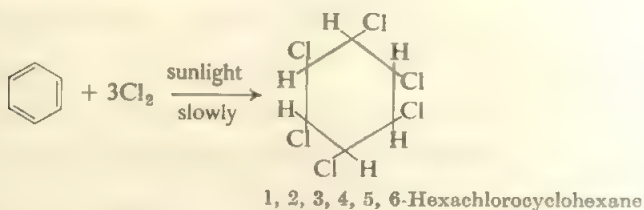
Benzene, as was pointed out in an earlier section, has a type of bonding that enables it to undergo certain reactions of both double and single bonded compounds. It adds hydrogen and chlorine in a reaction characteristic of unsaturated hydrocarbons; on the other hand, its most typical behavior is exhibited when it reacts by substitution to replace one or more of the hydrogen atoms present. Catalysts are commonly used to speed up and sometimes direct the course of the reactions which take place.

## A. ADDITION

(1) *Hydrogen* adds readily to benzene when heated (180–200°) with it in the presence of a nickel catalyst.



(2) The addition of *halogen* to benzene occurs and is favored by sunlight. Benzene adds chlorine in the presence of sunlight to form 1,2,3,4,5,6-hexachlorocyclohexane, a product which is sold commercially as Lindane or Benzenehexachloride, an insecticide.

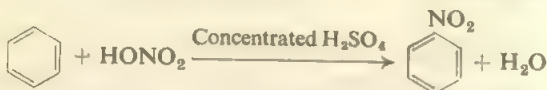


Bromine adds in a similar manner to form hexabromocyclohexane.

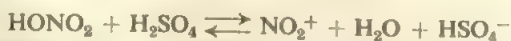
### B. SUBSTITUTION

Substitution is the more usual type of reaction shown by benzene and its homologs. Replacement of one or more hydrogens of benzene takes place when it reacts with halogens, nitric acid, sulfuric acid and alkyl halides under the right conditions and in the presence of suitable catalysts.

(1) **Nitration.** The substitution of a hydrogen atom attached to the aromatic nucleus of benzene by nitro groups is achieved through the use of concentrated nitric acid dissolved in concentrated sulfuric acid, a mixture sometimes referred to as "mixed acid." The monosubstitution product formed is nitrobenzene (oil of mirbane). The reaction is referred to as nitration.



Additional hydrogen atoms may be substituted if the temperature of the reaction mixture is raised somewhat and if a larger proportion of nitrating acid is used. Sulfuric acid has a dual function: It (a) acts as a water-absorbing agent and (b) reacts with the  $\text{HNO}_3$  to form  $\text{NO}_2^+$  (the nitronium ion), the species which appears to be the substituting reagent, although it is present in only very small amount in the nitric acid solution. It is formed by the reaction:



(2) **Sulfonation.** Benzene and related aromatic hydrocarbons react

with concentrated sulfuric acid itself to form sulfonic acids. Here a hydrogen atom or several hydrogens are replaced with the concurrent elimination of a molecule of water. This reaction is known as sulfonation.



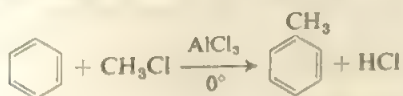
Here the sulfuric acid also has dual functions. Again, it acts as both (a) a water-absorbing agent and (b) the source of the  $\text{SO}_3$  (sulfur trioxide), which appears to be the substituting reagent of sulfuric acid.

Raising the temperature of the reaction permits the introduction of a second  $-\text{SO}_3\text{H}$  group into benzene. Other reagents, such as chlorosulfonic acid ( $\text{ClSO}_3\text{H}$ ), may also be used to introduce the sulfonic acid group.

(3) **Halogenation.** In the presence of iron or of its ferric salts, which act as catalysts, chlorine and bromine react readily with benzene to form chloro- or bromobenzene. Here a hydrogen atom is replaced with halogen and the reaction is known as halogenation. The reaction with chlorine is called chlorination; with bromine, bromination.

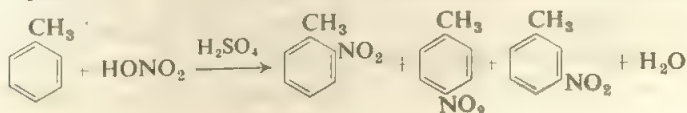


(4) **Alkylation (Friedel-Crafts reaction).** Alkyl halides in the presence of anhydrous aluminum chloride react with benzene to form alkyl substituted compounds in which an alkyl group is substituted for one or more hydrogen atoms. This reaction is spoken of as *alkylation*. According to the experimental conditions, mono-, di- or even trisubstituted benzenes may be obtained. The term Friedel-Crafts comes from the names of the two men, Charles Friedel and James M. Crafts, who discovered the reaction (1878). The aluminum chloride and other reagents, when used, must be dry:

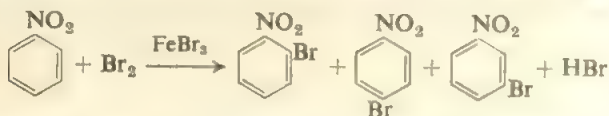


### C. DISUBSTITUTION

The introduction of a single atom or group into the benzene ring involves no uncertainty in predicting the structure of the product to be formed, since all the hydrogens which might be replaced are identical. Only one monosubstitution product is possible. The positions open to a second entering substituent indicate that at least three isomers may be formed. For example, the nitration of toluene indicates the possible formation of ortho-, meta- or paranitrotoluene disubstitution products. Likewise, when nitro-



benzene is brominated the possibility is open for the formation of ortho-, meta- or paranitrobromobenzene. Since three isomers are permitted in



both of these examples, the question might be asked, "Which of the possible products can one expect when di- or polysubstitution occurs?"

Experience has shown that the group, or groups, already present on the benzene ring determine the position taken by the next entering substituent. In the nitration of toluene, a mixture of o-nitrotoluene and p-nitrotoluene is obtained, accompanied by traces of m-nitrotoluene. On the other hand, bromination of nitrobenzene forms mainly m-bromonitrobenzene, with only small amounts of the ortho and para isomers.

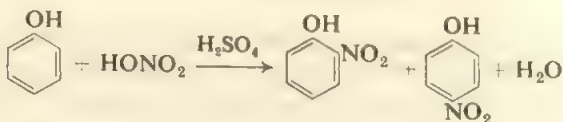
Such experiments show that the two groups induce the formation of differently positioned disubstitution products. This indicates that the group already attached to the ring has a marked directing effect. This directive phenomenon is referred to as *orientation* and the various types of substituents fall into two classes on the basis of their directive influence:

Class I: —OH, —NH<sub>2</sub>, —Cl, —Br, —I, —OR, —NHR, —NR<sub>2</sub>,  
—NHCOR, —R

Class II: —NH<sub>3</sub><sup>+</sup>, —NO<sub>2</sub>, —SO<sub>3</sub>H, —COOH, —CO<sub>2</sub>R, —CHO,  
—CN, —COCH<sub>3</sub>

Class I substituents direct the entering group to the ortho and para positions with respect to their location on the ring. Class II substituents direct the entering groups or atoms to the meta position with respect to themselves.

Application of these rules to a specific situation, the nitration of hydroxybenzene (phenol), leads one to predict that the products would be the ortho and para isomers. Experimental study of this reaction shows that actually about 40% of the o-nitrophenol and about 60% of p-nitrophenol are obtained.

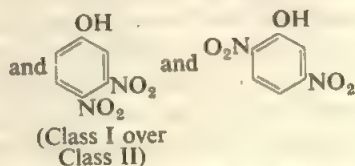
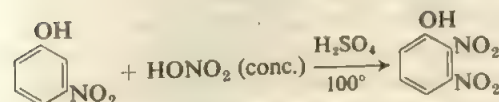
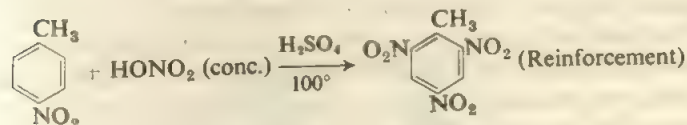
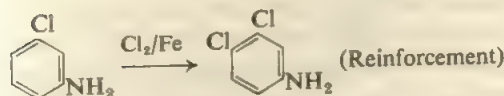
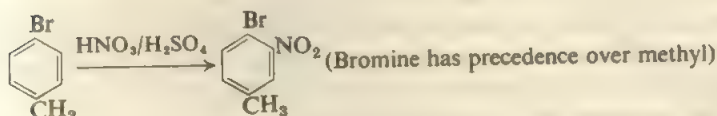
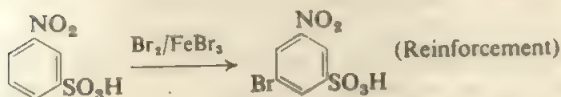
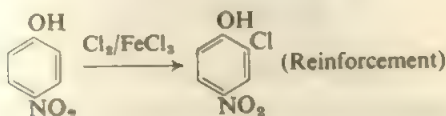


#### D. POLYSUBSTITUTION

The orientation of additional groups introduced into the benzene nucleus after two or more have already been substituted also depends upon the groups present. Where several groups are attached to the ring, they may reinforce if both direct substituents to the same locations, or they may oppose. Class I




groups take precedence over Class II groups in determining the position of the next entering substituent. Within each class, certain groups take precedence over others. The relative order of directive power for some Class I groups is  $-\text{OH} > -\text{NH}_2 > -\text{OR} > -\text{Cl} > -\text{Br} > -\text{I} > -\text{CH}_3$ . For Class II groups the relative order of directive influence is:  $-\text{NO}_2 > -\text{SO}_3\text{H} > -\text{CN} > -\text{COOH}$ . The following reactions illustrate the application of these findings to particular compounds:



### E. ACTIVATION AND DEACTIVATION

The presence of substituents on an aromatic ring, in addition to their directing influence, also modifies the ease with which further substitution takes place. Those groups which make substitution easier are said to be "activating." Groups which hinder further substitution are said to be "deactivating." Class I substituents, with the single exception of the halogens, are

activating and when present make subsequent substitutions easier. For example, phenol, —OH, reacts with nitric acid much faster and more readily than does benzene. Class II substituents deactivate the aromatic ring. Nitrobenzene is much more difficult to nitrate than is benzene. Halogens deactivate the ring to further substitution, but still remain ortho-para directing. In general, further substitution reactions of derivatives having ortho-para directing groups proceed more readily than do substitutions of the parent hydrocarbon.

#### F. THEORETICAL

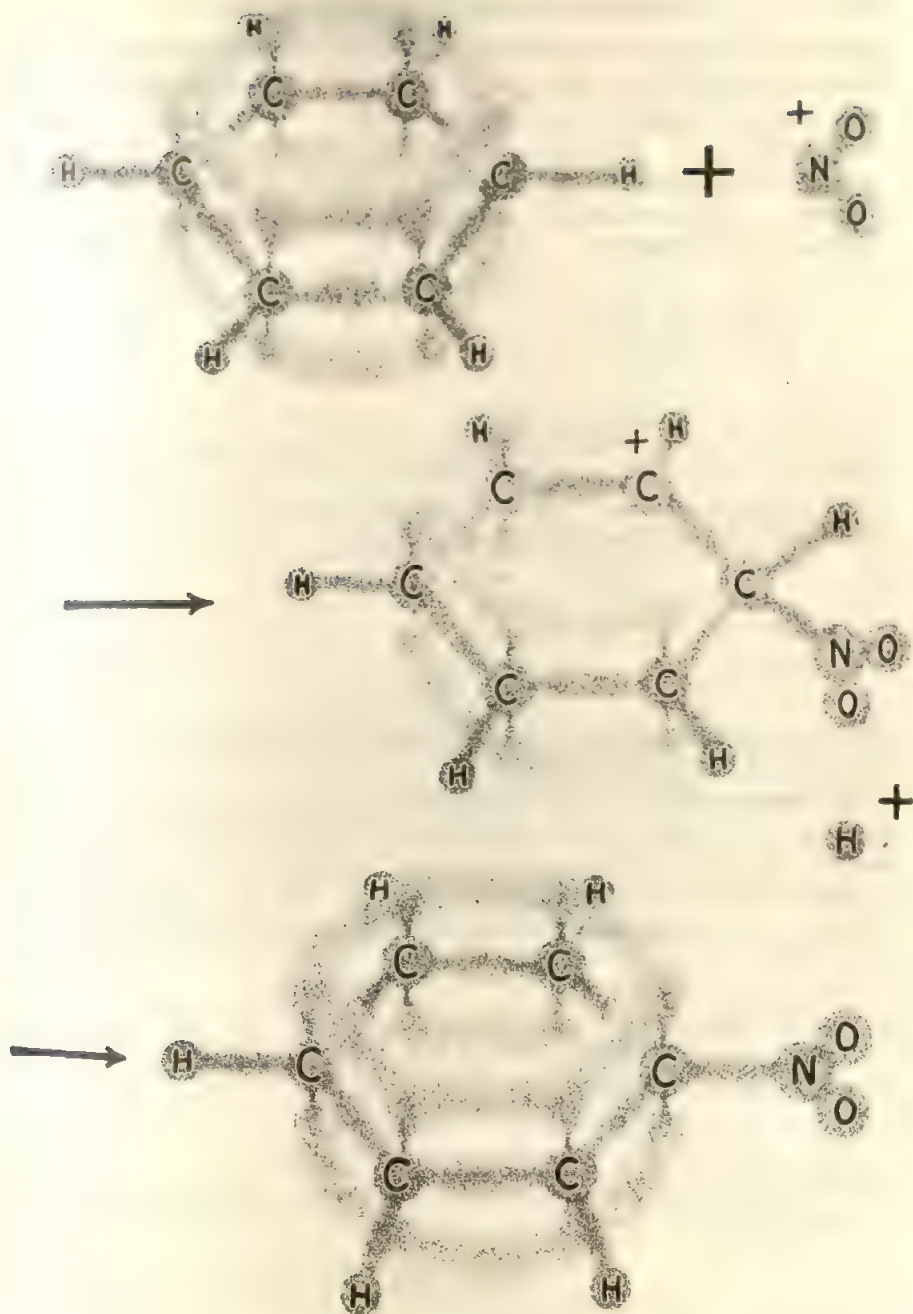
An explanation for the substitution reactions of benzene and other aromatic hydrocarbons can be found through an examination of their electronic structures. Benzene has six electrons (pi electrons) which are more exposed to the action of reagents than are electrons of saturated compounds. These electrons, however, are not so available to attack as are those of alkenes or alkynes because of mutual interaction (resonance) which results in their stabilization. Like the alkenes, benzene has a negative character due to its exposed pi electrons. It reacts much as does ethylene by shifting its more mobile electrons on demand of an approaching positive reagent to form a dipolar structure on two adjacent carbons.

On this basis, substitution reactions of benzene may be pictured as proceeding according to a sequence which involves (1) the approach of a positively charged ion or dipolar ion, and the polarization of a benzene carbon-carbon bond (the distortion of the pi orbitals) under the influence of the approaching reagent, (2) the union of the positive reagent with the negative end of the polarized carbon-carbon bond to form an unstable structure which stabilizes itself by (3) the loss of a proton from the carbon to which the substituting reagent adds. Nitration occurs as shown in Figure 31.6.

Since there is general agreement that aromatic substitution proceeds by attack of a positive ion, it follows that any attached group which tends to increase the electron density in the ring should increase the rate of substitution. Likewise, a group which decreases the electron density should cause substitution to occur more slowly. Activation can therefore be explained by assuming that the ortho-para directing groups (Class I), with the exception of the halogens, raise the electron density of the ring. A theoretical interpretation which explains both the orientation and the activating-deactivating effects of various substituents is thus achieved. From this explanation of activation and deactivation, it would appear clear why Class I substituents almost always take precedence over Class II groups in cases where they compete in determining the orientation of the next entering group. The Class I groups act to assist the reaction rather than to hinder it, as is the case for meta directing groups.

#### G. SEVERAL REACTIONS OF ALKYL BENZENES

As shown in an earlier paragraph, the Friedel-Crafts reaction produces a



In Kekulé notation:

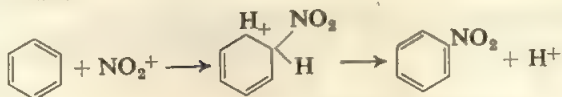
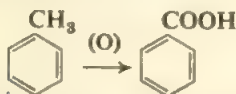


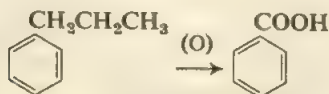
Figure 31.6. The mechanism for the nitration of benzene.

hydrocarbon derivative of benzene, toluene, which is composed of two parts, an aromatic (aryl) and an alkyl group. Reaction of compounds of this type may take place in either or both of these groups.

(1) **Oxidation.** With toluene, which has an alkyl group attached to the ring, oxidation affects the alkyl without transforming the aromatic ring. Toluene is readily oxidized to benzoic acid with oxidizing agents such as potassium permanganate:

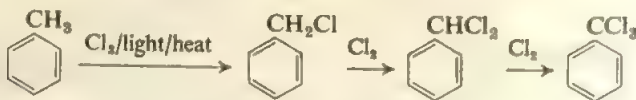


Since alkanes are not oxidized readily under these same conditions, the aryl group must have had a modifying influence on the alkyl group, making it more subject to oxidation. When a longer alkyl group is present, oxidation also takes place with formation of benzoic acid.



The ring in either case resists oxidation under these conditions, showing its inherently large degree of stability.


(2) **Halogenation** of toluene is dependent upon the conditions. When benzene is chlorinated at low temperatures in the presence of a catalyst, substitution occurs on the ring as expected. At higher temperatures, when a catalyst is not used, substitution occurs in the side-chain methyl group. Mono-, di- or trisubstitution occurs, depending on the conditions and reaction time.



The methyl group attached to the ring does not react with either nitric acid or sulfuric acid.

### EXERCISES

1. Define: (a) aromatic character, (b) unsaturation, (c) saturation, (d) resonance, (e) orientation.
2. Which of these molecules are planar: (a)  $\text{C}_2\text{H}_2\text{Cl}_2$ , (b)  $\text{CH}_2\text{Cl}_2$ , (c)  $\text{C}_2\text{H}_2$ , (d)  $\text{C}_2\text{H}_4$ , (e)  $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ , (f)  $\text{C}_6\text{H}_6$ , (g)  $\text{C}_{10}\text{H}_8$  (naphthalene), (h)  $\text{C}_6\text{H}_6\text{Cl}_6$  (1,2,3,4,5,6-hexachlorocyclohexane)?

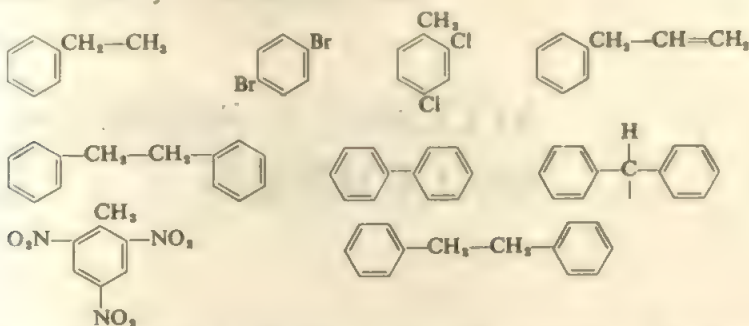
3. Criticize  as a symbol for benzene.



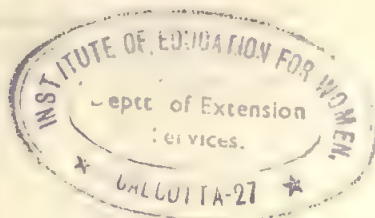
4. Describe the following structural features of benzene:

- $C-C-C$  bond angle
- $H-C-C$  bond angle
- $C-H$  bond length
- $C-C$  bond length.

5. Name each of these by two correct IUPAC names:



- Write an equation showing the conversion of benzene to cyclohexane. Show catalyst and special conditions over the arrow.
- Write equations showing catalysts and special conditions for
  - the alkylation of toluene
  - the nitration of toluene
  - the sulfonation of toluene
  - the substitution of halogens on the ring of toluene.
- Explain ortho-para and meta direction.
- Write formulas for 5 meta and for 6 ortho-para directing groups.
- Explain activation and deactivation as related to o-p and m- directing groups.
- Write equations including OVER the ARROW special conditions and catalysts for
  - the preparations of methylcyclohexane from benzene (2 steps)
  - the preparation of m-chloronitrobenzene from benzene (2 steps)
  - benzoic acid from benzene (2 steps).



# ALCOHOLS, PHENOLS AND ETHERS

Oxygen is found in more organic compounds than any other element, except the ever present carbon and hydrogen. It is a constituent of many types of compounds, among which are alcohols, phenols, ethers, aldehydes, ketones, acids, carbohydrates and fats. Many individual compounds are found widely distributed in nature, many are of great biological significance and many have important industrial uses. Several chapters shall be devoted to the study of oxygen-containing compounds.

## 1. STRUCTURE VERSUS PHYSICAL PROPERTIES

In this chapter compounds in which oxygen has two single bonds will be studied. In one respect these compounds are similar to water. Oxygen has two single bonds in the water molecule (Fig. 32.1). With the two hydrogens

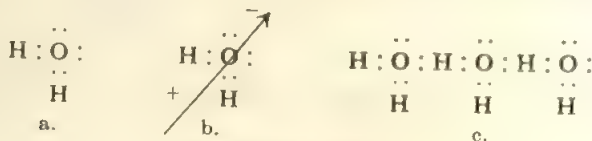
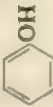
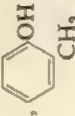


Figure 32.1. Water.

attached by single bonds, the molecule is bent at the oxygen; the angle between the two bonds is  $104^\circ$ , very near the tetrahedral angle. Because oxygen is much more electronegative than hydrogen, the molecule is highly polar, and adjacent molecules can cling together by *hydrogen bonding*. This is relatively weak bonding by which the hydrogen is held between negative electrons of the oxygens of adjacent water molecules.

Table 32.1. Physical Properties of Some Alcohols, Phenols and Ethers

Name	Formula	Melting Point °C	Boiling Point °C	Density	Solubility g/100 g Water
Methyl alcohol	CH <sub>3</sub> OH	-97.8	64.6	0.796	Completely
Ethyl alcohol	CH <sub>3</sub> CH <sub>2</sub> OH	-117	78.5	0.789	Completely
Isopropyl alcohol	(CH <sub>3</sub> ) <sub>2</sub> CHOH	-88	82.3	0.785	Completely
n-Butyl alcohol	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> OH	-89	118	0.810	7.9
n-Hexyl alcohol	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> OH	-51	157.2	0.819	0.59
2,3-Hexanediol	CH <sub>3</sub> (CHOH) <sub>2</sub> (CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub>	—	207	0.967	Completely
Phenol	C <sub>6</sub> H <sub>5</sub> OH, 	41	182	1.07	6.7
o-Cresol	o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> OH, 	30	191.5	1.05	3.1
Dimethyl ether	CH <sub>3</sub> -O-CH <sub>3</sub>	-138.5	-24	—	Very soluble
Ethylmethyl ether	CH <sub>3</sub> CH <sub>2</sub> -O-CH <sub>3</sub>	—	7.9	0.726	Soluble
Ethyl ether, Diethyl ether	CH <sub>3</sub> CH <sub>2</sub> -O-CH <sub>2</sub> CH <sub>3</sub>	-116	34.6	0.713	7.5

Alcohols, phenols and ethers are bent molecules (Fig. 32.2):

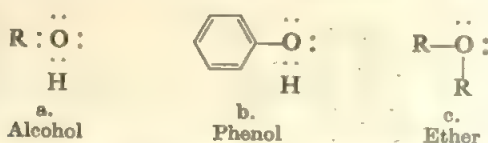


Figure 32.2. Alcohol, phenol, ether.

One might consider an alcohol to be a derivative of water in which one of the hydrogens is replaced by an alkyl group: methyl, ethyl, etc. In phenol one hydrogen is replaced by an aromatic group (that is, the -OH group is attached to a carbon of an aromatic ring). In an ether, both hydrogens of water are replaced by alkyl or aryl groups. Obviously the properties of water are retained in greater degree in phenols and alcohols in which only one hydrogen is lost. Like water, an alcohol molecule is polar (but less polar than water) (Fig. 32.3a).

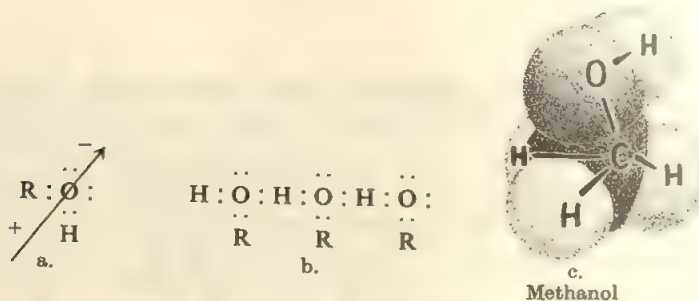
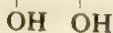


Figure 32.3. Alcohol.

The polarity is greatest for the smallest members, methyl and ethyl alcohols. Hydrogen bonding is significant among the smaller members (Fig. 32.3b). The increased attraction of the molecules for one another and for other polar molecules, owing to the functional hydroxyl group ( $\text{-OH}$ ), tends to increase both the boiling points and the solubilities of the alcohols in water. None of the alcohols are gases at room temperature, despite the fact that the smallest, methyl alcohol ( $\text{CH}_3\text{OH}$ ), has nearly the same molecular weight as ethane gas. Furthermore, the first four members are completely soluble in water. All hydrocarbons are insoluble. The alcohols are less dense than water. Physical properties of some alcohols are shown in Table 32.1.

A study of this table shows that alcohols containing up to three carbon atoms are completely soluble in water. With more carbons the solubility decreases rapidly, unless there are more  $\text{-OH}$  groups. 2,3-Hexanediol,  $\text{CH}_3\text{-CH(OH)-CH(OH)-CH}_2\text{-CH}_2\text{-CH}_3$ , is completely soluble. Usually poly-



alcohols are soluble, unless the carbon to hydroxyl ratio exceeds three.



Alcohols are, in a sense, part alkane and part water. The presence of the alkyl group makes them solvents for alkane-like substances. They are used as solvents for organic chemicals. Many drugs which are insoluble in water because of their organic character are prepared and used in alcohol solutions called *tinctures*. Because of the polar hydroxyl group, smaller members of the alcohol series are soluble in water. These alcohols are often used as solvents to bring water and water insoluble organic material together.

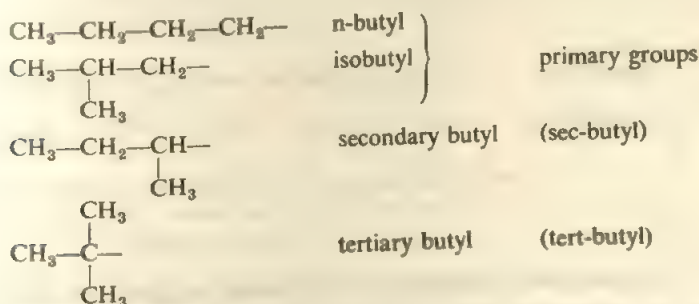
As shown in the table, the phenols with the compact aromatic ring have a density greater than water. They are solids and are only sparingly soluble in water.

The presence of the oxygen atom has a smaller influence on properties of ethers when the oxygen is between two alkyl groups. The polarity effect is present in smaller molecules, but hydrogen bonding cannot exist. As seen in Table 32.1, the first two members (up to three carbons) are gases at room temperature and are very soluble in water. Diethyl ether with four carbons, having the same molecular weight as n-butyl alcohol, has nearly the same solubility in water as n-butyl alcohol, but it is much more volatile. Its boiling point is 34°C compared to 118°C for n-butyl alcohol.

## 2. ALCOHOLS

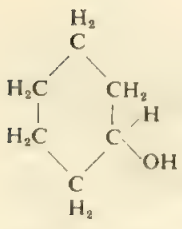
### A. NOMENCLATURE

Many alcohols are best known by common names which are obtained by adding the term alcohol to the name of the alkyl group attached to the hydroxyl group. The common names of some alcohols appear in Table 32.2. At this point one should be familiar with all the alkyl groups named in this table, except those of the amyl alcohols, which are only specific names, and the butyl (four carbon) alcohols.



Secondary and tertiary have further significance in classifying all alkyl groups. Although neither n-butyl nor isobutyl is called primary butyl alcohol, both are primary alcohols. The terms primary, secondary and tertiary refer to the number of alkyl carbons to which the carbon bearing the functional group is attached; primary indicates that the carbon is attached to one other (or none other); secondary, to two other carbons; and tertiary, to

Table 32.2. Names of Some Alcohols

Formula	Common Name	IUPAC Name
$\text{CH}_3\text{OH}$	Methyl alcohol	Methanol
$\text{CH}_3\text{—CH}_2\text{OH}$	Ethyl alcohol	Ethanol
$\text{CH}_3\text{—CH}_2\text{—CH}_2\text{OH}$	n-Propyl alcohol	1-Propanol
$\begin{array}{c} \text{CH}_3\text{—CH—OH} \\   \\ \text{CH}_3 \end{array}$	Isopropyl alcohol	2-Propanol
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	n-Butyl alcohol	1-Butanol
$\begin{array}{c} \text{CH}_3\text{—CH}_2\text{—CHOH} \\   \\ \text{CH}_3 \end{array}$	Sec-butyl alcohol	2-Butanol
$\begin{array}{c} \text{CH}_3\text{—CH—CH}_2\text{OH} \\   \\ \text{CH}_3 \end{array}$	Isobutyl alcohol	2-Methyl-1-propanol
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3\text{—C—OH} \\   \\ \text{CH}_3 \end{array}$	Tert-butyl alcohol	2-Methyl-2-propanol
$\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—OH}$	n-Amyl alcohol	1-Pentanol
$\begin{array}{c} \text{CH}_3\text{—CH—CH}_2\text{—CH}_2\text{—OH} \\   \\ \text{CH}_3 \end{array}$	Isoamyl alcohol	3-Methyl-1-butanol
	Cyclohexyl alcohol	Cyclohexanol

three. Alcohols and other series of compounds are also classified primary, secondary and tertiary by the structure of the carbon to which the functional group is attached. The distinction is useful, because these classes often act differently.

The IUPAC rules may be extended to alcohols with one hydroxyl group ( $\text{—OH}$ ) as follows:

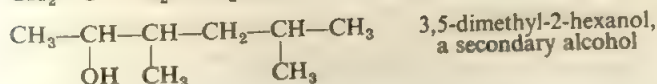
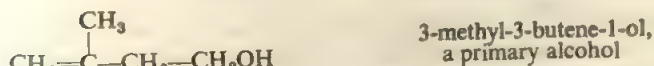
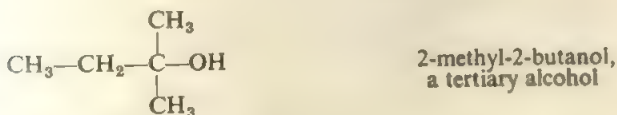
(1) Choose the longest carbon chain, including the carbon attached to the hydroxyl group.

(2) Name the chain as an alkane, but change the name ending by replacing *e* with *ol*. Officially, alcohols are alkanols.

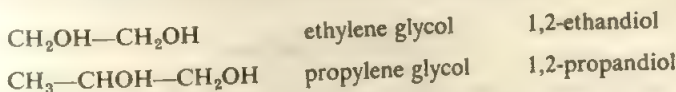
(3) Number the chain to give the carbon with the hydroxyl group the lowest number. The OH group takes precedence in numbering over any multiple bond that may be present.

(4) Name all branches in alphabetical order and indicate the position of attachment with preceding numbers as before. Check the IUPAC names appearing in Table 32.2 for agreement with the rules.

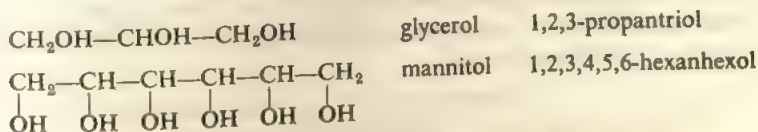
Other examples are:



Alcohols having more than one hydroxyl group are commonly known as di-, tri- or polyhydroxy alcohols. They are officially known as diols, triols or polyols. Some common polyols are:



Both glycols (diols) are used as permanent antifreezes.

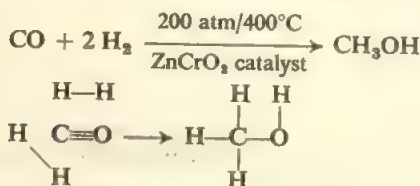


## B. PREPARATION

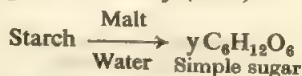
Alcohols may be prepared in a variety of ways, including specific methods applicable for the preparation of only the particular alcohol concerned, as well as general methods for preparing a series of alcohols.

## (1) SPECIFIC METHODS

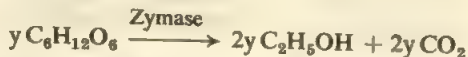
(a) *Methyl alcohol (methanol)*, the simplest of the alcohols, is obtained commercially from hydrogen and carbon monoxide, using a specific catalytic process. In this method, water gas (a mixture of carbon monoxide and hydrogen formed by spraying hot coke with steam), with some added hydrogen, is forced at high pressure (200 atmospheres) over zinc chromite catalyst at a temperature near 400°C.



(b) *Ethyl alcohol (ethanol)*, another very common and widely used alcohol, is obtained by a specific procedure known as fermentation. In this method, sugar is transformed into ethyl alcohol and carbon dioxide under the influence of a mixture of biological catalysts called enzymes which are found in, and formed by, growing yeast cells. The mixture of yeast enzymes is called "zymase." Commercially, starch and "black strap molasses" are used as starting materials. Starch is first converted into sugar by an enzyme found in freshly sprouted barley (malt):



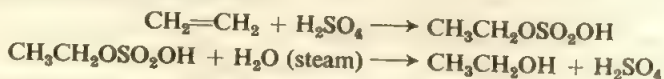
where  $y$  is any number.



Fermentation of sugar to produce ethanol is only one example of a large number of industrial processes which utilize fermentation. Many antibiotics such as penicillin and hormones such as cortisone, along with a variety of other substances, are obtained commercially by fermentation methods.

## (2) GENERAL METHODS

(a) *Ethyl alcohol* is also prepared from ethylene by a strictly chemical procedure. This method involves the addition of sulfuric acid, followed by hydrolysis of the addition product with steam. Since ethylene is obtained from the cracking of petroleum, ethyl alcohol plants are often built in the vicinity of petroleum plants.

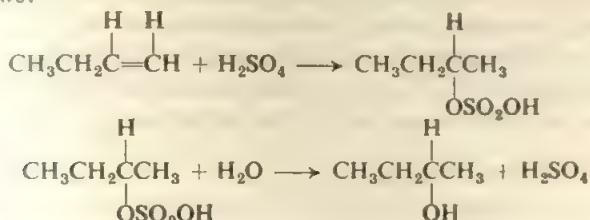


The reaction of sulfuric acid with alkenes followed by hydrolysis is a general method for the preparation of secondary alcohols. Note that the addition of sulfuric acid to alkenes places the  $-\text{OSO}_2\text{OH}$  group in such a position (Markownikoff's rule) that it always\* forms a secondary or tertiary alcohol

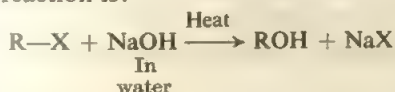
\* Except in the case of ethylene.



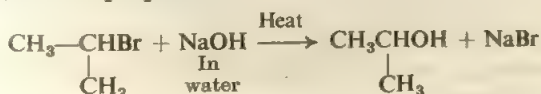
when hydrolyzed. The formation of 2-butanol from 1-butene is accomplished as follows:



(b) The *alkaline* hydrolysis of alkyl halides is a general laboratory method for preparing alcohols. In practice the alkyl halide (haloalkane) is heated with a concentrated aqueous (water) solution of sodium hydroxide. The general reaction is:



where X represents any halogen and R— represents any alkyl group. The specific reaction for the preparation of isopropyl alcohol from isopropyl bromide (2-bromopropane) is:



The method is best for the preparation of primary alcohols from primary alkyl halides; secondary and tertiary alkyl halides react more slowly. With tertiary alkyl halides, a considerable quantity of alkene is formed. The reason is apparent when one considers the course of the reaction. The attacking species is the hydroxide ion. This negative ion approaches the carbon to which the negative halogen is attached from the side opposite the halogen. The hydroxide ion forms a bond with the carbon, at the same time freeing the bromide ion on the opposite side. Figure 32.4a illustrates the process with ethyl bromide and hydroxide ion.

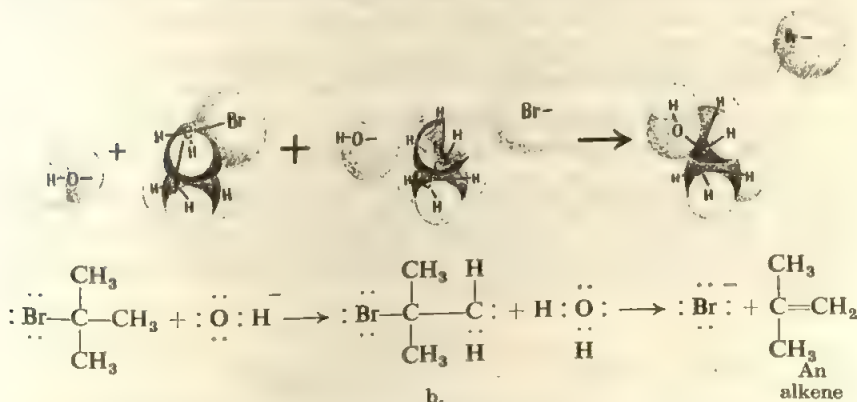


Figure 32.4. Comparison of reaction of ethyl bromide and t-butylbromide with hydroxide ion.

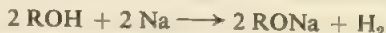
When the hydroxide ion approaches tertiary butyl bromide, it encounters difficulty in reaching the tertiary carbon imbedded in the center of the molecule. Instead, some hydroxide ions draw a charged hydrogen (a proton) from one of the  $\text{CH}_3$ — groups. The unshared pair of electrons on the  $\text{CH}_2$  group shifts inside to form a double bond and the bromide ion is eliminated (Fig. 32.4b). A reaction of this type is referred to as an elimination reaction.

### C. REACTIONS

The hydroxyl group is responsible for the characteristic behavior of alcohols. At least four types of reactions are common to alcohols. These include reactions which result in: (1) replacement of the hydrogen atom of the hydroxyl group, (2) replacement of the  $-\text{OH}$  group itself through cleavage of the alcohol carbon-oxygen bond, (3) dehydration of the alcohol and (4) oxidation of the alcohol to an aldehyde, ketone or carboxylic acid.

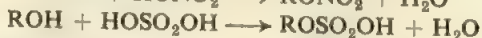
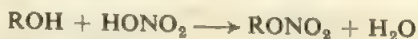
#### (1) REPLACEMENT OF THE HYDROGEN OF THE $-\text{OH}$ GROUP

(a) The hydrogen of the hydroxyl groups of alcohols reacts quite differently from other hydrogens present in the molecule. It is weakly acidic, much less acidic than water in fact. It is not acidic enough to react with strong bases such as sodium hydroxide, but it is replaced slowly with sodium or potassium metal, liberating hydrogen.

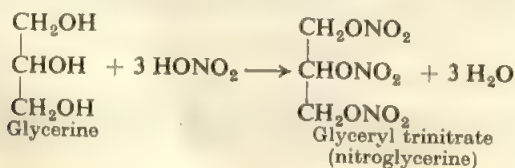


Primary alcohols react most rapidly; the tertiary reacts least rapidly. The alkoxide formed decomposes with water to reform the alcohol and liberate sodium hydroxide. The recommended method for the disposal of sodium metal wastes is to dissolve them in alcohol in which the sodium reacts slowly.

(b) Alcohols react with hydroxyl-containing strong acids such as  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  to form esters. An ester is the other product formed when an H from the hydroxyl group of the alcohol combines with the  $-\text{OH}$  group of an acid to form water. The net result is replacement of the H of the alcohol  $-\text{OH}$  with  $-\text{NO}_2$  or  $-\text{SO}_3\text{H}$ , depending on the inorganic acid used. Instead of an  $-\text{OH}$  attached to the R, one now finds an  $-\text{ONO}_2$  or  $-\text{OSO}_3\text{H}$ .



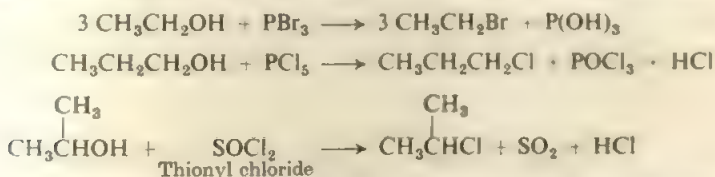
The reaction of alcohols with nitric acid has wide application in the manufacture of explosives. For example, nitroglycerin, which structurally is glyceryl trinitrate, is formed when glycerol reacts with either concentrated or dilute nitric acid at low temperature:



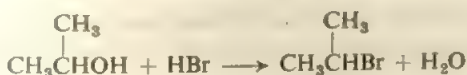
Gun cotton, another useful explosive, results from the reaction between cellulose (in cotton), a polyhydroxy compound and nitric acid. Esters of other inorganic acids include those of nitrous acid and phosphoric acid. Esters of phosphoric acid are of particular importance in life processes. Glucose (see Chapter 40), the sugar which is used for energy by most living organisms, is utilized by them only after its conversion into an ester of phosphoric acid. Unless combined with phosphoric acid in the cell it is not useful to them.

## (2) REPLACEMENT OF THE —OH GROUP

(a) Typical of reactions of this type is the replacement of —OH with a halogen atom as a result of the reaction with *phosphorus trichloride*, *tribromide* or *triiodide*, or with *phosphorus pentachloride* or *thionyl chloride*:



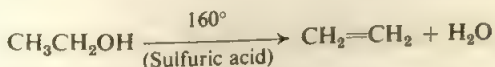
(b) Reaction with *hydrohalic acids* also replaces an —OH group with a halogen atom. HBr, HI and HCl react to produce alkyl halides. The reaction between HBr and 2-propanol is as follows:



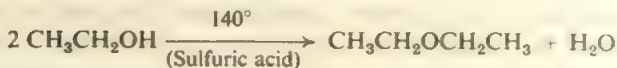
The order of reactivity of alcohols toward replacement of the hydroxyl group with a halogen by a given hydrohalic acid is  $\text{R}_3\text{COH} > \text{R}_2\text{CHOH} > \text{RCH}_2\text{OH}$ . The use of the Lucas reagent, which is a mixture of concentrated HCl in zinc chloride solution, is based on this difference in reactivity. Tertiary alcohols react rapidly with the reagent, secondary alcohols react slowly and primary alcohols hardly at all, even when heated. The order of reactivity of the hydrohalic acids with respect to replacement of the —OH group is  $\text{HI} > \text{HBr} > \text{HCl}$ .

## (3) DEHYDRATION OF ALCOHOLS (REMOVAL OF WATER)

Monohydroxy alcohols lose water under the proper experimental conditions in the presence of dehydrating agents to yield ethers or alkenes. The dehydration of ethanol is a classical reaction which may be used to illustrate the transformations which are likely. When ethanol is heated to a relatively high temperature ( $160^\circ\text{C}$ ) in the presence of concentrated sulfuric acid, a dehydrating agent, ethylene, is obtained as a result of intramolecular loss of water.



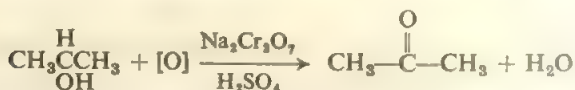
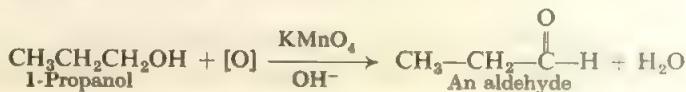
At a lower temperature and with the ratio of alcohol to sulfuric acid markedly increased, diethyl ether is obtained as the principal product.



Here intermolecular loss of water takes place. Secondary alcohols dehydrate more readily than do primary alcohols. Tertiary alcohols dehydrate intramolecularly so easily that tertiary alkyl ethers are seldom obtained. Special methods are used to obtain ethers from tertiary alcohols and from some secondary alcohols.

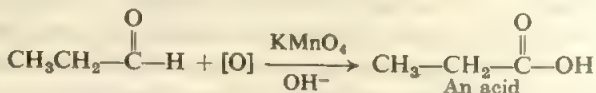
#### (4) OXIDATION OF ALCOHOLS

Primary and secondary alcohols are readily oxidized to aldehydes and ketones:

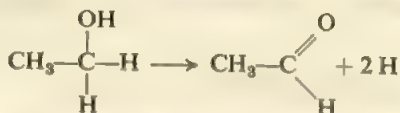


These equations are not balanced. The symbol [O] is used to indicate that oxygen is gained from an oxidizing agent. The notation  $\xrightarrow[\text{OH}^-]{\text{KMnO}_4}$  indicates that the oxidizing agent is a basic potassium permanganate solution.

Unless the aldehyde is removed from the oxidizing solution, it is oxidized further to a carboxylic acid:



The oxidation of primary and secondary alcohols to aldehydes and ketones amounts to a dehydrogenation:



A tertiary alcohol has no hydrogen on the carbon to which the hydroxyl group is attached and cannot be oxidized in this manner. However, under vigorous conditions tertiary alcohols undergo oxidative degradation to form compounds having fewer carbon atoms than the alcohol. Some of the products obtained when tertiary butyl alcohol is heated for several hours with an

acid solution of sodium dichromate are: acetic acid ( $\text{CH}_3\text{—}\overset{\text{O}}{\parallel}\text{C—OH}$ ),

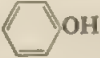

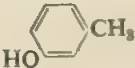



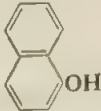
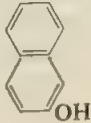
acetone ( $\text{CH}_3\text{—}\overset{\text{O}}{\parallel}\text{C—CH}_3$ ), carbon dioxide and water.



## 3. PHENOLS

A phenol is a compound containing a hydroxyl group attached to a carbon of an aromatic (benzene-like) ring. Several phenols and their common and official names are listed in Table 32.3. Phenols may be classified as mono-, di- or tri-hydroxy phenols, depending on the number of —OH groups attached to aromatic rings. They are named as hydroxy derivatives of the aromatic hydrocarbon to which they are attached. Observe the names given in Table 32.3.

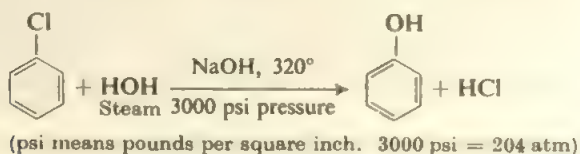
Table 32.3. Names and Structures of Some Phenols

<i>Name</i>	<i>Structure</i>	<i>IUPAC Name</i>
Phenol		Hydroxy benzene
o-Cresol		2-Hydroxy toluene
m-Cresol		3-Hydroxy toluene
p-Cresol		4-Hydroxy toluene
Resorcinol		1,3-Dihydroxybenzene
Hydroquinone		1,4-Dihydroxybenzene
$\alpha$ -Naphthol		1-Hydroxy naphthalene
$\beta$ -Naphthol		2-Hydroxy naphthalene

## A. PREPARATION OF PHENOLS

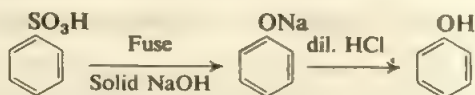
Two of several methods for obtaining phenols should be mentioned. Both involve the replacement of an atom already attached to the aromatic ring with a hydroxyl group.

(1) Although replacement of a halogen attached directly to an aromatic ring is usually very difficult, phenol itself is prepared industrially by the *hydrolysis of chlorobenzene* under extreme conditions of temperature and pressure.



The slightly acidic phenol is obtained in the highly alkaline medium as the sodium salt which is converted into phenol upon acidification.

(2) The second method of fairly general application is the *fusion of the salt of the aromatic sulfonic acid* (see Chapter 34) with solid sodium hydroxide. During fusion the sulfonic acid group is replaced with a hydroxyl group. The resulting phenol in the highly basic medium appears as its sodium salt, from which the phenol is liberated by adding acid. When benzenesulfonic acid, obtained from the sulfonation of benzene, is fused with sodium hydroxide, and the fusion mixture is acidified, the reaction sequence which takes place is:



Phenols are isolated from coal tar by extraction and distillation procedures.

## B. REACTIONS

Functional groups directly attached to an aromatic ring frequently exhibit unique behavior. This becomes apparent when the chemical behavior of phenols is compared with that of the alcohols. Although phenols and alcohols form many similar derivatives, these are often prepared using quite different procedures and reagents. Of the four types of alcohol reactions discussed in the previous paragraphs only the following two are of any real importance for phenols: (1) The hydrogen of the —OH of phenols is subject to replacement much as in the case of the alcohols. The replacement of the —OH group with other atoms or groups and dehydration do not occur with phenols. (2) Ready oxidation is characteristic of phenols.

Substitution of other atoms or groups in place of hydrogen atoms of the aromatic ring is also characteristic of phenols.

### (1) REPLACEMENT OF THE HYDROGEN OF THE PHENOLIC —OH GROUP (NEUTRALIZATION OR SALT FORMATION)

The hydrogen of the —OH group in phenols is more acidic than is the corresponding hydrogen of alcohols. Phenols therefore react with sodium or potassium metal as do alcohols, but in addition are sufficiently acidic to

undergo neutralization with aqueous solutions of sodium hydroxide (or other strong bases):

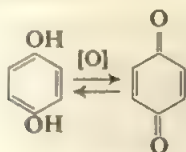


The resulting sodium phenoxide salt is soluble in water. Because of this reaction phenols are soluble in a sodium hydroxide solution.

Phenols however are weaker acids than carbonic acid and do not dissolve in sodium carbonate solutions. The formation of soluble salts with sodium hydroxide permits the separation of phenols from non-acidic, water-insoluble organic compounds.

## (2) OXIDATION

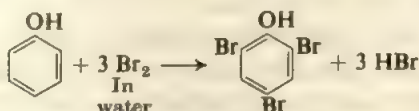
Phenols are readily oxidized and yield a variety of complex products. Vigorous oxidation results in cleavage of the carbon ring, yielding carboxylic acids and other products. Controlled oxidation of certain polyhydric phenols is possible. For example, hydroquinone is readily transformed into p-benzoquinone.



The ease with which hydroquinone undergoes oxidation makes it valuable as an antioxidant since it reacts readily with and destroys a variety of substances which catalyze the oxidative decomposition of organic substances.

## (3) RING SUBSTITUTION

Phenols undergo the usual substitution reactions characteristic of aromatic hydrocarbons. Since the hydroxyl group is a strong ortho-para directing group (a ring-activating group) phenol substitutions occur more readily than for the corresponding hydrocarbon. In fact, ease of substitution is one of the distinguishing characteristics of phenols. The rapid reaction of phenol with bromine which occurs in the absence of the usual catalyst (carrier) is an excellent example. A precipitate of 2,4,6-tribromophenol appears very rapidly when phenol is added to bromine water.



It is not possible to form monobromophenol by direct bromination.

Dilute nitric acid alone readily reacts with phenol to form a mixture of ortho- and para-nitrophenols (Chapter 31), although much oxidation occurs





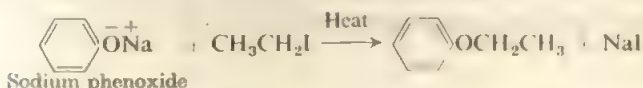
oxygen are alkyl groups (Fig. 32.5a, b, c) the ether may be represented by  $R-O-R'$  and called an aliphatic ether. When at least one group is attached to the oxygen through carbon of a benzene type ring, the ether is an aromatic ether (Fig. 32.5c, d).

### A. PREPARATION OF ETHERS

Ethers may be prepared by the dehydration of alcohols with sulfuric acid (noted earlier in this chapter). Another useful synthesis is the Williamson synthesis, in which an alkoxide (a sodium salt of an alcohol) reacts with an alkyl halide. In the preparation of diethyl ether, ethyl bromide is allowed to react with sodium ethoxide,  $NaOCH_2CH_3$ .



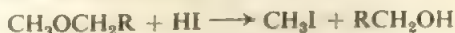
Similarly, for preparing phenetole (phenyl ethyl ether), one permits sodium phenoxide to react with ethyl iodide,



The experimental conditions for carrying out this reaction with various other phenols and alkyl halides differ widely and are determined by the reactivity of the substances employed. This reaction has particular advantage for the preparation of mixed ethers.

### B. REACTIONS OF ETHERS

Ethers are isomeric with alcohols. Diethyl ether and n-butyl alcohol have the same molecular formula. Methyl ethyl ether has the same molecular formula as n-propyl alcohol. Chemically the isomers are very different. Alcohols are much more reactive than are ethers. Ethers do not react with alkali metals such as sodium, nor with strong bases and oxidizing agents. They are similar chemically to the paraffins. However, they are soluble in concentrated sulfuric acid, a characteristic of most oxygen-containing compounds. By this reaction, ethers can be readily distinguished from hydrocarbons. Ethers are cleaved by hot concentrated mineral acids. The reaction which occurs may be written as follows:

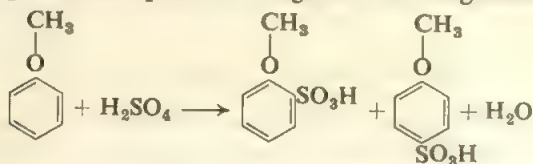


The most effective acid for this transformation is concentrated hydriodic acid.

With excess HI, the alcohol formed in the above case is converted into the corresponding alkyl iodide. Cleavage of ethers with HBr proceeds more slowly and requires higher temperatures. However, phenetole (phenyl ethyl ether) may be cleaved with HBr to yield phenol:



Alkyl aryl ethers are sufficiently stable in the presence of acids to permit normal substitution reactions of the aromatic ring. Since the —OR group is activating and ortho-para directing, the following reaction can be expected:



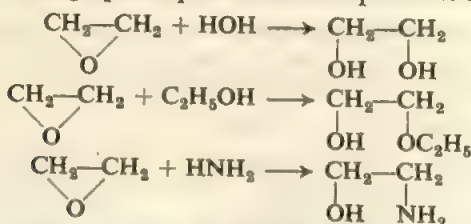
The ethers are one of the less important classes of organic compounds and are used chiefly as solvents. Diethyl ether, probably the most widely used compound of this class, is employed in extracting fats from biological materials. It is also used as a general anesthetic.

### C. SPECIAL ETHERS—ALKENE OXIDES

In addition to the more conventional ethers which have just been discussed, alkene oxides should be mentioned. Ethylene oxide,  $\text{CH}_2\text{—CH}_2$ , is the



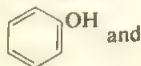
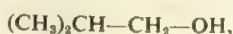
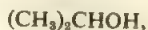
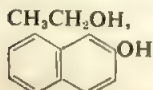
simplest example of a compound of this class. Oxides of this type are highly reactive cyclic ethers whose behavior is said to be due to the internal strain common to three-membered ring systems. Alkene oxides react rapidly with many reagents, in the course of which reactions the three-membered ring is opened, relieving the strain. This is illustrated by reactions of ethylene oxide with water, methanol and ammonia. Note that in each case the three-membered ring opens up, and addition products are obtained.



The commercial importance of ethylene oxide is dependent upon this remarkable reactivity, which permits its ready conversion into many useful compounds.

### EXERCISES

- Which elements are necessarily found in alcohols?
- Define and give an example of each by writing the formula: (a) primary alcohol, (b) secondary alcohol, (c) tertiary alcohol, (d) phenol, (e) simple ether, (f) aromatic ether, (g) alkene oxide.
- Write both the correct common names and the IUPAC names for  $\text{CH}_3\text{OH}$ ,



4. Define the term functional group. What is the functional group in  $\text{CH}_3\text{—CH}_2\text{—CH—(CH}_3\text{)OH}$ ? What function does it perform when sodium metal is dropped into the anhydrous alcohol?
5. Give the order of reactivity of primary, secondary and tertiary alcohols and phenols with: (a) sodium metal, (b) hydrohalic acids, (c) concentrated sulfuric acid (intramolecular dehydration), (d) oxidation with basic potassium permanganate solution, (e) neutralization with aqueous sodium hydroxide.
6. Write balanced equations showing reaction conditions over the arrow for the reaction of bromine water: (a) with propane in the dark, (b) with propylene in the dark, (c) with phenol.
7. Describe a chemical method for separating the components of a solution of phenol in cyclohexanol.
8. Write structural formulas for each of seven compounds with the formula  $\text{C}_4\text{H}_{10}\text{O}$ .
9. In what way is the Williamson synthesis superior to dehydration with sulfuric acid in preparing mixed ethers?
10. Write equations for the reaction of concentrated hydroiodic acid with methylethylether.
11. Write equations for the two-step preparation of: (a) dimethyl ether, starting with carbon monoxide and steam, (b) methyl isopropyl ether from the two alcohols, (c) isopropyl alcohol from propene.
12. Bottles, each containing one of the liquids 1-pentyne, 2-pentyne, secondary butyl alcohol, n-hexane and methyl n-propyl ether, are unlabeled. Describe how you would identify each chemically for labeling.

ALDEHYDES AND  
KETONES

The study of aldehydes and ketones is the study of the carbonyl group, its chemical reactivity and the reactivity of neighboring atoms in the molecule.

## 1. THE CARBONYL GROUP

The carbonyl functional group is a carbon atom and an oxygen atom joined together by a double bond. The next neighboring atoms are either two carbons, in which case the compound is a ketone, or a carbon and a hydrogen, which give an aldehyde. In the one compound, formaldehyde, the simplest of carbonyl compounds, the carbonyl group is flanked by two hydrogens. Formaldehyde may be represented in several ways (Fig. 33.1).

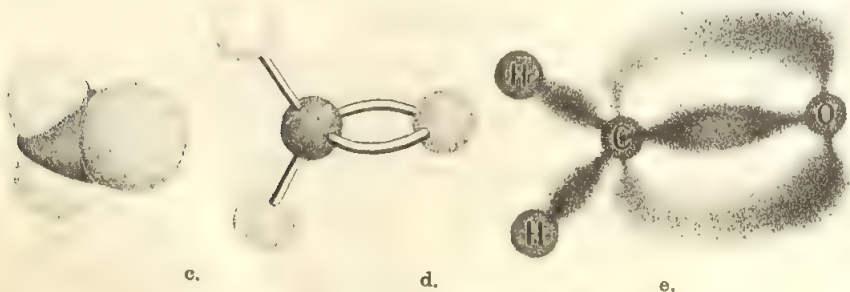
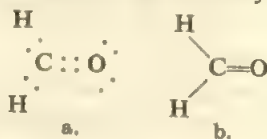


Figure 33.1. Formaldehyde.



The electron configuration (a) shows that each atom has the inert gas configuration by sharing. The bond structure which appears in (b) shows single carbon to hydrogen bonds and a double carbon to oxygen bond. In (d) the double bond appears as it would if two single bonds from each atom were drawn together. The molecular orbital representation is shown in (e). Two electrons of those linking carbon to oxygen occupy a sigma ( $\sigma$ ) orbital directly between the two atoms. A pi ( $\pi$ ) orbital shown above and below the sigma bond contains the second pair of electrons. As with the pi electrons of the double carbon to carbon bond; these pi electrons are more exposed and are affected to greater extent by approaching particles than are sigma electrons. The double carbon to oxygen bond differs in one important respect from the double carbon to carbon bond. The C to O linkage is highly polar, the oxygen atom being more electronegative than the carbon. Compared to one another, carbon is positive and oxygen is negative.

Figure 33.2 shows two methods for representing the three dimensional structure of acetaldehyde.

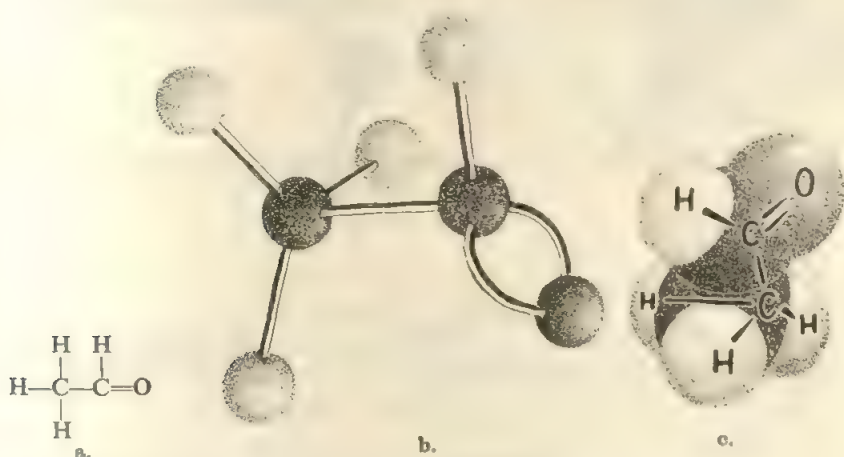


Figure 33.2. Acetaldehyde.

## 2. NOMENCLATURE

### A. ALDEHYDES

To be attached to both another carbon and a hydrogen, the carbon of the carbonyl group of an aldehyde must be terminal (that is, it must be the end carbon). Some common aldehydes are listed in Table 33.1.

Common names of aldehydes are derived from the common names of acids differing only in the functional group. Formic acid has the same number of carbons as formaldehyde; acetic acid, as acetaldehyde; cinnamic acid, as cinnamaldehyde, etc. (Chapter 34). Aldehydes may be either *aromatic* or *aliphatic*. The carbonyl group of an aromatic aldehyde must be attached directly to a carbon of a benzene or benzene-like ring. Of those illustrated in

Table 33.1. Common Aldehydes

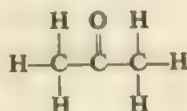
Formula	Common Name	IUPAC Name
$\begin{array}{c} \text{H} \\   \\ \text{C}=\text{O} \text{ (CH}_2\text{O)} \\   \\ \text{H} \end{array}$	Formaldehyde	Methanal
$\begin{array}{c} \text{O} \\    \\ \text{CH}_3-\text{C} \text{ (CH}_3\text{CHO)} \\   \\ \text{H} \end{array}$	Acetaldehyde	Ethanal
$\begin{array}{c} \text{O} \\    \\ \text{C}_6\text{H}_5-\text{C} \text{ (C}_6\text{H}_5\text{CHO)} \\   \\ \text{H} \end{array}$	Benzaldehyde	Phenylmethanal
$\begin{array}{c} \text{O} \\    \\ \text{C}_6\text{H}_5-\text{CH}=\text{CH}-\text{CH} \end{array}$	Cinnamaldehyde	3-Phenyl-2-propenal
$\begin{array}{c} \text{O} \\    \\ \text{C}-\text{H} \\   \\ \text{C}_6\text{H}_4(\text{OH})(\text{OCH}_3) \end{array}$	Vanillin	(4-Hydroxy-3-methoxyphenyl)methanal
$\begin{array}{c} \text{CH}_3 \quad \text{O} \\   \quad    \\ \text{CH}_3-\text{CH}-\text{CH} \text{ ((CH}_3\text{)}_2\text{CHCHO)} \end{array}$	Isobutyraldehyde	2-Methylpropanal

Table 33.1, only benzaldehyde and vanillin are aromatic. If the carbonyl group is not attached directly to an *aromatic* carbon, the aldehyde is *aliphatic*.

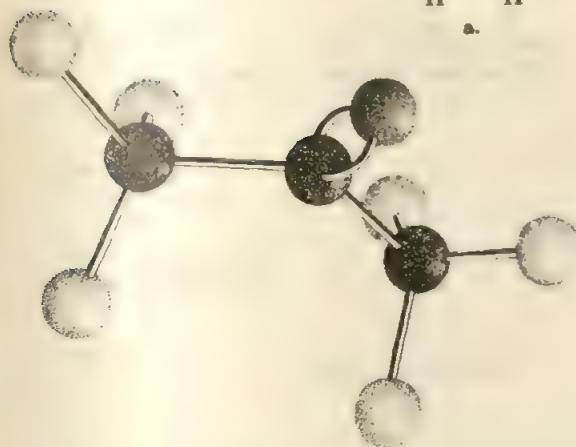
The IUPAC name ending for aldehydes is *al*, which replaces the *e* in *aliphatic* (straight chain hydrocarbon) names. For naming, the carbon of the carbonyl group must be included in the primary chain of carbons, and it becomes carbon *number one*. Because the carbonyl carbon is *number one*, its position need not be specified with a number. In other respects aldehydes are named as other organic compounds. Compare the IUPAC names in Table 33.1 with the structural formulas.

## B. KETONES

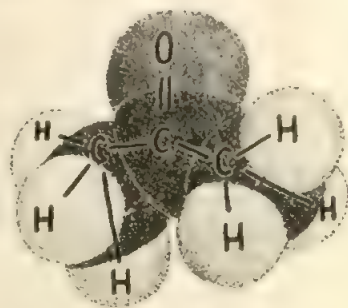
Because the carbonyl group of a ketone is attached to *two* carbons, ketones may be either *aliphatic*, *aromatic* or *mixed aliphatic and aromatic*. Figure 33.3 (compare with Fig. 33.2) illustrates the three dimensional structure of acetone. Of the compounds listed in Table 33.2 only benzophenone is aromatic; acetophenone and benzylphenylketone are mixed aromatic-aliphatic; and the balance are aliphatic ketones.



a.



b.

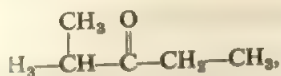


c.

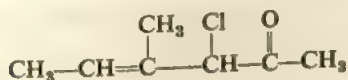
Figure 33.3. Acetone.

Most common names of ketones follow a system similar to that used for naming ethers. The names of both groups attached to the carbonyl group are followed by the word ketone (Table 33.2). The IUPAC name ending for ketones is *one*, which replaces the *e* of aliphatic hydrocarbon names. The carbon of the carbonyl group must be contained in the primary carbon chain. Its position in the chain is indicated by number. In other respects, ketones are named according to the system for other organic compounds.

Isopropylethylketone,

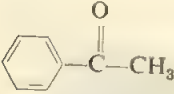
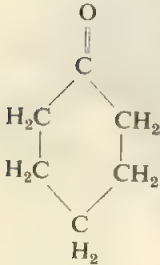
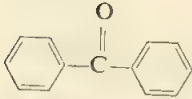
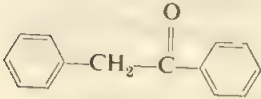


is named 2-methyl-3-pentanone. The compound



is named 3-chloro-4-methyl-4-hexen-2-one.

Table 33.2. Some Ketones

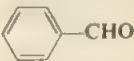
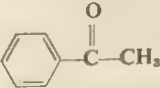
Formula	Common Name	IUPAC Name
$\text{CH}_3-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_3$	Acetone, Dimethylketone	Propanone
$\text{CH}_3-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_2-\text{CH}_3$	Methylethylketone	2-Butanone
	Acetophenone, Phenylmethylketone	1-Phenylethanone
	—	Cyclohexanone
	Benzophenone	Diphenylmethanone
	Benzylphenylketone	1,2-Diphenylethanone

### 3. PHYSICAL PROPERTIES

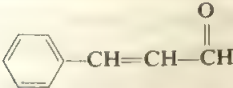
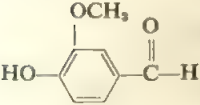
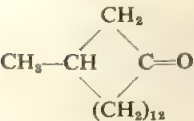
The presence of the polar carbonyl group increases the attraction of molecules of carbonyl compounds for one another and for polar water molecules. As a result, the boiling points of these compounds are considerably higher than the boiling points of hydrocarbons with nearly the same molecular weight. Formaldehyde and acetaldehyde are the only gases at room temperature. The smaller carbonyl compounds, *up to 2 or 3 carbons*, are completely soluble in water. Solubility in both polar and non-polar solvents makes acetone a very useful solvent.



**Table 33.3. Physical Properties of Some Aldehydes and Ketones**

Name	Formula	Boiling Point, °C	Density	Solubility in Water, Grams per 100 g Water
Formaldehyde (Methanal)	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}-\text{C}-\text{H} \end{array}$	-21	0.815	Completely soluble
Acetaldehyde (Ethanal)	$\text{CH}_3\text{CHO}$	20.2	0.7834	Completely soluble
Propionaldehyde (Propanal)	$\text{CH}_3\text{CH}_2\text{CHO}$	48.8	0.807	20
n-Butyraldehyde (Butanal)	$\text{CH}_3(\text{CH}_2)_3\text{CHO}$	75.7	0.817	3.7
Benzaldehyde (Phenylmethanal)		179.6	1.050	0.33
Acetone (Propanone)	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3-\text{C}-\text{CH}_3 \end{array}$	56.5	0.792	Completely soluble
2-Butanone	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3-\text{C}-\text{CH}_2-\text{CH}_3 \end{array}$	79.6	0.805	35.3
Acetophenone (1-Phenylethanone)		202.3	1.036	Insoluble

**Table 33.4. Odors of Some Compounds**

Formula	Name	Odor
	Cinnamaldehyde	Cinnamon
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3-\text{C}=\text{CH}-\text{CH}_2-\text{CH}_2-\text{C}(\text{CH}_3)=\text{CH}-\text{C}(=\text{O})-\text{H} \end{array}$	Citral	Lemon
	Vanillin	Vanilla
	Muscone	Musk

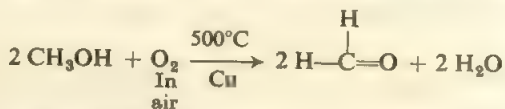
Many aldehydes and ketones have distinctive odors. In addition to having an acrid odor, formaldehyde vapors temporarily destroy the sense of smell. Table 33.4 gives the odors of some carbonyl compounds.

#### 4. PREPARATION

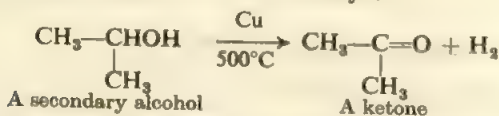
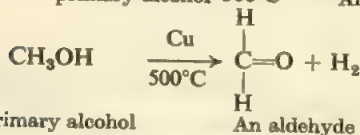
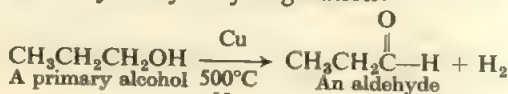
Aldehydes and ketones may be prepared in several ways. Four of the most significant methods will be noted here.

A. The *oxidation of primary alcohols to yield aldehydes* and the attendant problem of further oxidation were discussed under reactions of alcohols (Chapter 32). The oxidation of *secondary alcohols to prepare ketones* was discussed in the same chapter.

A specific oxidation of a primary alcohol of industrial importance is the vapor phase oxidation of methanol with air over a hot copper catalyst.

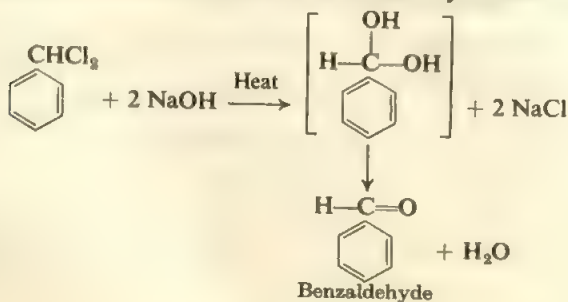


B. *Carbonyl compounds can be prepared by dehydrogenation.* Using the same alcohols and the same catalysts as are used in oxidation, one can form ketones and aldehydes by dehydrogenation:



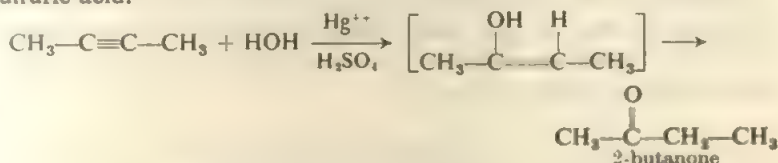
The oxidation of methanol with air, and dehydrogenation, both with a hot copper catalyst, are the two principal methods for producing formaldehyde.

C. Aldehydes and ketones may be obtained by *hydrolysis of alkyl dihalides* (dihaloalkanes) in which both halogen groups are on the same carbon. Consider the hydrolysis of dichlorophenylmethane (benzal chloride) when it is heated with an aqueous solution of sodium hydroxide:



An alkyl halide may be converted to an alcohol (the halide being replaced by the hydroxyl group) by heating with an aqueous solution of a strong base. In this case replacement of the two halides leaves two hydroxyl groups on the same carbon. Such a structure, shown within the brackets in the equation, is unstable, decomposing to an aldehyde by loss of water. An aldehyde was formed in this example because the two halogens appeared on a *terminal* carbon. Were both halogens on a non-terminal carbon, hydrolysis would yield a ketone.

D. The fourth method, *addition of water to an acetylenic compound*, was discussed as a reaction of multiple carbon to carbon bonds. The preparation of acetaldehyde was demonstrated there. 2-Butanone can be prepared by addition of water to 2-butyne in the presence of a solution of mercuric sulfate and sulfuric acid.



## 5. REACTIONS

Because the carbon to oxygen bond is both polar and unsaturated, the carbonyl group is very active chemically toward addition of either polar or ionic substances. Its polarity makes it attractive to other polar molecules and to ions; its pi bonds yield to addition. Identification of addition products reveals that the positive portion of the adding compound becomes attached to the oxygen; the negative portion to the carbon. Furthermore, experimental studies indicate that the negative portion adds to the carbon of the carbonyl first. Accordingly, the addition of hydrocyanic acid (HCN) to acetaldehyde would occur as shown in Figure 33.4.

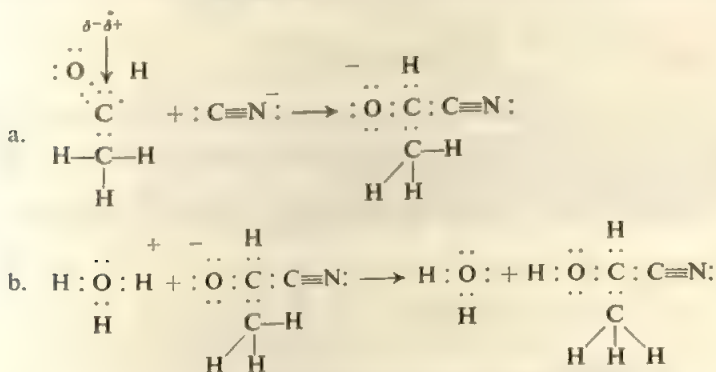
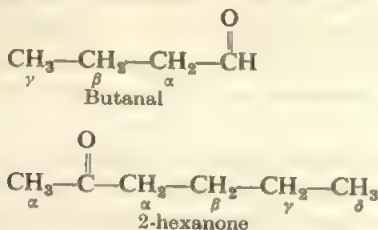


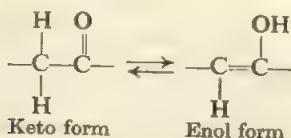
Figure 33.4. Course of addition of hydrocyanic acid to acetaldehyde.

Other atoms of aldehydes and ketones are affected by the presence of the carbonyl group. Among those most influenced are the  $\alpha$ -hydrogens, the bond between them and the carbon being weakened by the carbonyl group.

An  $\alpha$ -hydrogen is a hydrogen attached to an  $\alpha$ -carbon, one adjacent to the functional group. The carbons of butanal and 2-hexanone are labeled with letters of the Greek alphabet:



Beginning at the carbon adjacent to the carbonyl group, the carbons are designated in order as alpha, beta, gamma and delta. The weakening of the  $\alpha$ -hydrogen bond is seen in the fact that ketones and aldehydes exist in an enol form as well as in a keto form.



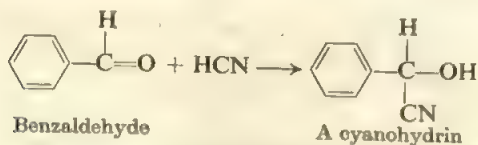
In effect an  $\alpha$ -hydrogen migrates to the oxygen of the carbonyl group from the  $\alpha$ -carbon to give the enol. Actually the  $\alpha$ -hydrogen is lost and another is gained by the oxygen. An equilibrium exists between these two forms. With most compounds the equilibrium, as illustrated above, is far to the left.

Reactions of aldehydes and ketones are largely those of addition to the carbonyl group, loss of an active hydrogen, oxidation (aldehydes), and directed substitution (aromatic aldehydes and ketones).

### A. ADDITION REACTIONS

Some reagents which add to the carbonyl group are hydrocyanic acid, water, alcohols, bisulfite ion, ammonia and ammonia-like compounds. Aldehydes and ketones may even add to themselves.

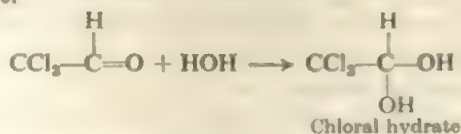
(1) *Hydrogen cyanide* (hydrocyanic acid) adds to give a cyanohydrin.



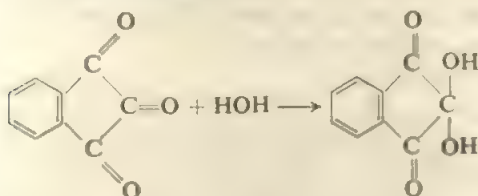
(2) *Water* adds to only a few aldehydes and ketones to give stable hydrates. One preparation of carbonyl compounds, the hydrolysis of dihalides, depends on the general *instability* of the hydrates.



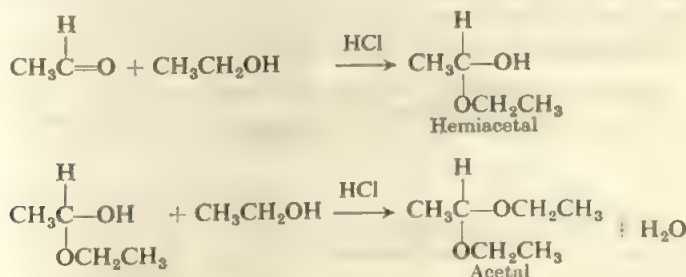
(a) *Chloral* (2,2,2-trichloroethanal) adds water to give stable chloral hydrate, the principal ingredient of "knock-out drops," a narcotic and hypnotic.



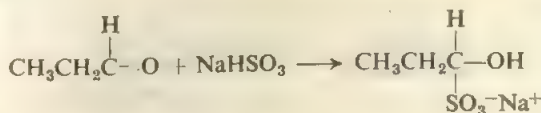
(b) *Ninhydrin*, used in the identification and analysis of proteins, is a triketone which adds water.



(3) *Addition of alcohol.* Many alcohols add to the carbonyl group of aldehydes in the presence of suitable acid catalysts to form hemiacetals. Hemiacetals are unstable but may be stabilized by further reaction with alcohol to form acetals. Most ketones do not readily undergo this direct reaction. Benzaldehyde diethyl acetal (b.p. 222°) can be prepared in 55% yield by direct reaction in the presence of dry hydrogen chloride. With acetaldehyde the reaction is

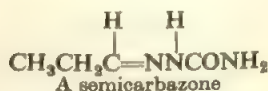
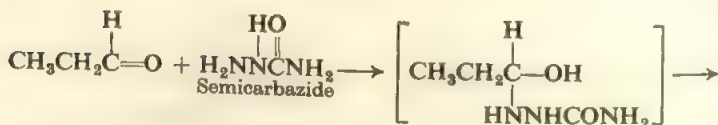
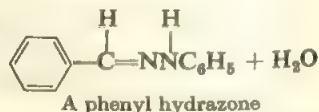
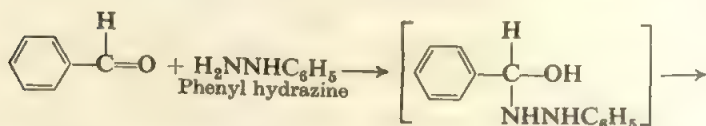
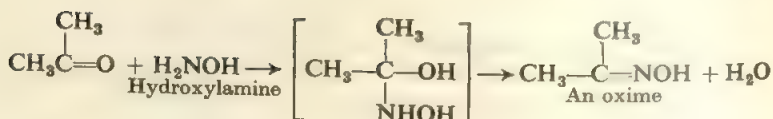
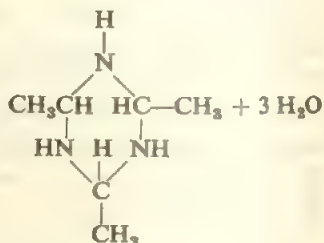
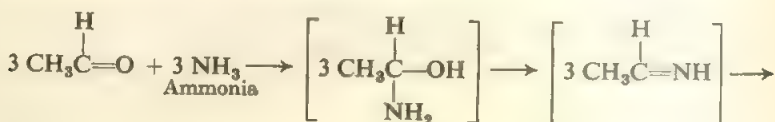


(4) *Addition of sodium bisulfite.* Sodium bisulfite ( $\text{NaHSO}_3$ ) reacts with most aldehydes, methyl alkyl ketones and non-aromatic cyclic ketones to form slightly soluble solid "bisulfite addition" products. The reaction with propanal is:



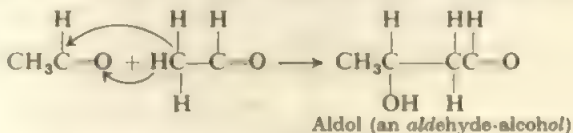
Since the addition products are readily decomposed by either acid or alkali, the reaction serves as a convenient means of separating and recovering aldehydes or ketones from accompanying impurities.

(5) *Addition of ammonia and ammonia derivatives.* Ammonia and its derivatives, hydroxyl amine ( $\text{H}_2\text{NOH}$ ), phenyl hydrazine ( $\text{C}_6\text{H}_5\text{NHNH}_2$ ), and semicarbazide ( $\text{H}_2\text{NCONHNH}_2$ ), each have a free pair of electrons bound to nitrogen. These electrons are available to bond with the carbon of the carbonyl group of aldehydes and ketones. The addition products, however, are unstable reactive substances which, in most cases, lose water immediately. The compounds obtained as a result of this loss of water are stable crystalline materials which have proved to be very useful for the characterization and identification of carbonyl-containing compounds. In the case of ammonia, the dehydration products are not usually obtained because, in most cases, they polymerize to form *cyclic trimers*. Representative equations for reactions of this type follow:

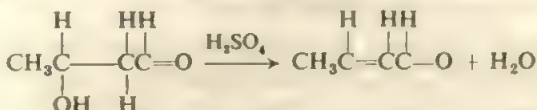


The substances given in the brackets are not usually isolated, but are the presumed reaction intermediates. The net result of these reactions is a substitution of a nitrogen compound for the oxygen of the carbonyl group.

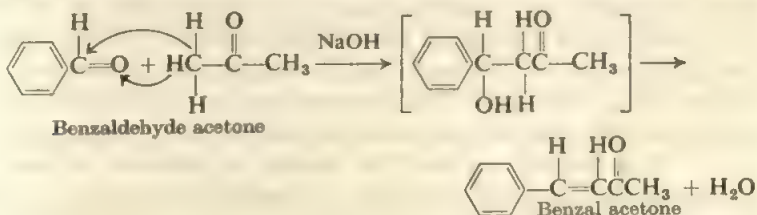
(6) *Self addition.* Self addition results from the presence of less strongly bonded  $\alpha$ -hydrogen atoms. Self additions of aldehydes and ketones are, in general, referred to as *aldol condensations*. The term aldol condensation is taken from the name given to the specific product, aldol, formed when acetaldehyde reacts with itself in the presence of dilute alkali.



Sometimes the addition products are stable enough to be isolated. In other cases water may be lost spontaneously to form unsaturated aldehydes or ketones. Aldol itself may be isolated, but it does undergo dehydration, forming crotonaldehyde when the solution is acidified with sulfuric acid.

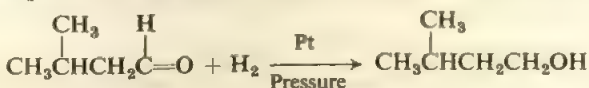


Ketones exhibit a smaller tendency to undergo the aldol condensation than do the aldehydes. Aromatic aldehydes possess no  $\alpha$  hydrogens and can not undergo the aldol condensation. They do, however, form aldol-type condensation products with other compounds which have  $\alpha$ -hydrogen atoms. For example, acetone reacts to form benzal acetone by the reaction:

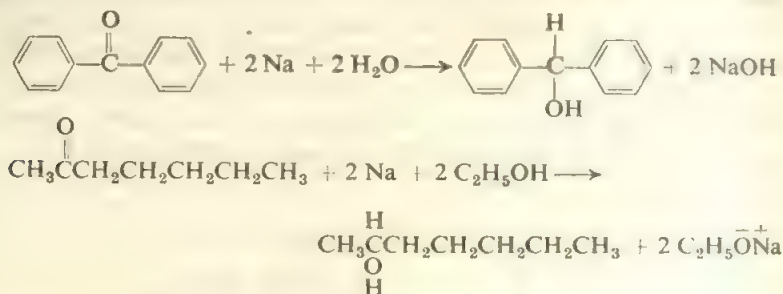


Self addition does not always stop with the completion of one step. If a large number of molecules combine together as a result of a sequence of aldol condensations, viscous, water-insoluble materials known as resins or polymers are formed.

(7) *Reduction.* Reduction, although considered separately from other addition reactions since it is due to a different mechanism, is really the simplest of all additions. Most aldehydes and ketones add hydrogen directly to the carbonyl to form alcohols, provided suitable catalysts such as platinum, palladium, nickel or copper chromite are provided.



The reduction of the carbonyl group may also be accomplished with chemical reducing agents such as sodium amalgam in water or sodium metal in ethanol.

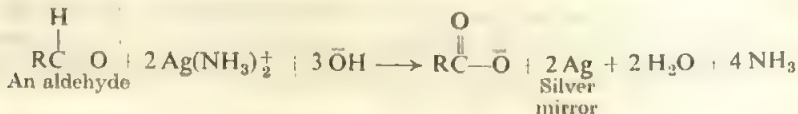


This reaction is a reversal of the dehydrogenation of alcohols (discussed in an earlier section) as a method for preparing aldehydes or ketones.

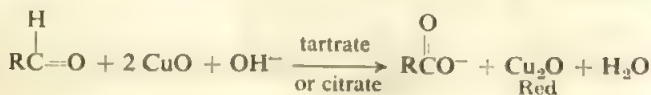
### B. OXIDATION

One of the important differences between aldehydes and ketones is their relative ease of oxidation. Aldehydes are oxidized very readily. Ketones undergo oxidation only with strong oxidizing agents under rather unusual conditions. The difficulty in the oxidation of ketones is understood when one realizes the carbon to carbon bonds must be broken, degrading the compound into fragments, all of which have fewer atoms than the original ketone.

Several tests based on this difference in behavior are used to distinguish aldehydes from ketones. Very mild oxidizing agents such as *Tollens' reagent*, *Fehling's solution* and *Benedict's solution*, too mild to affect the oxidation of either multiple C to C bonds or alcohols, can be used for this purpose because they do not react with ketones. Tollens' reagent is an ammoniacal solution of silver nitrate. Reaction with this reagent converts an aldehyde to a salt of a carboxylic acid, and the silver ammonia complex ion is reduced to metallic silver. If the test tube in which the reaction is performed is clean, a silver mirror will form on the glass surface. A simplified equation for this reaction is:



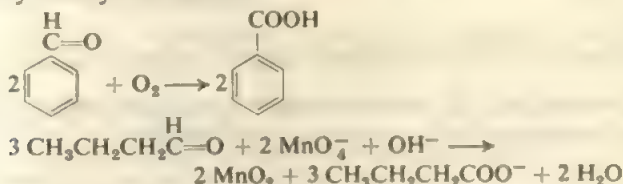
Fehling's and Benedict's reagents are alkaline solutions of cupric sulfate with a suitable binding reagent (called a chelating agent) added to keep the cupric ion in solution. Sodium citrate serves this function in Benedict's solution. The equation for the reaction may be written as:





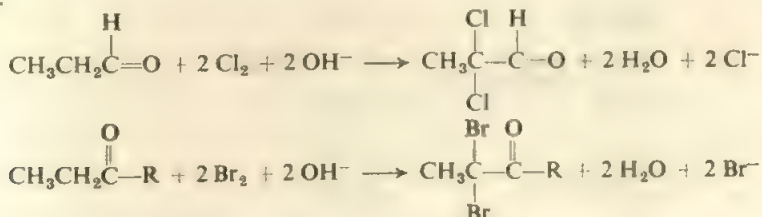
The occurrence of a reaction when this test is performed is shown by the appearance of cuprous oxide as a red precipitate. This reaction is often used to detect the presence of an amount of a "reducing" sugar in the blood or urine. The quantity of cuprous oxide formed is a measure of the sugar concentration. Benedict's and Fehling's solutions do not oxidize aromatic aldehydes like benzaldehyde, whereas Tollens' reagent does.

With stronger oxidizing agents, aldehydes are oxidized readily to the corresponding carboxylic acids or their salts. Both aromatic and alkyl aldehydes react smoothly with alkaline potassium dichromate, alkaline potassium permanganate, hydrogen peroxide, aqueous silver oxide, peracetic acid and oxygen. These reactions may be illustrated by the oxidation of benzaldehyde and *n*-butyraldehyde as follows:



### C. SUBSTITUTION OF ALPHA HYDROGENS

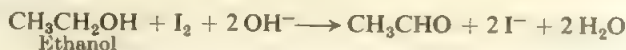
Hydrogen atoms attached to the  $\alpha$ -carbon of aldehydes and ketones may be readily replaced by halogen atoms in a basic solution. One or more such atoms may be substituted, depending on the time and conditions under which the reaction is performed. The equation for this reaction may be written as follows:



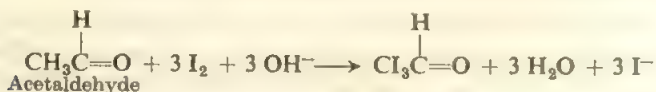
When acetaldehyde reacts with chlorine in a basic solution, three  $\alpha$ -hydrogens are replaced to form chloral (2,2,2-trichloroethanal). Substances of this type, that is, compounds having three halogens substituted on a carbon next to a carbonyl, are readily cleaved with the alkali present. The carbon-carbon bond of chloral breaks to form chloroform ( $\text{CHCl}_3$ ). Iodoform, a yellow crystalline solid, precipitates when acetaldehyde reacts under similar conditions with iodine in an alkaline solution. This reaction with a basic solution of iodine, called the *iodoform test*, is used to detect acetaldehyde,

methyl ketones or potential methyl ketones. The structure  $\text{CH}_3\overset{\text{O}}{\underset{||}{\text{C}}}-$  is needed, because the basic cleavage occurs only after  $\text{Cl}_3\text{C}-$  forms. Ethanol

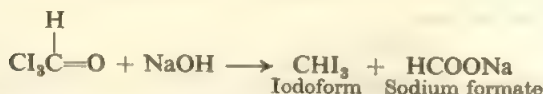
gives a positive iodoform test, because the reagent itself oxidizes ethanol to acetaldehyde.



Replacement of the active alpha-hydrogens with iodine follows:



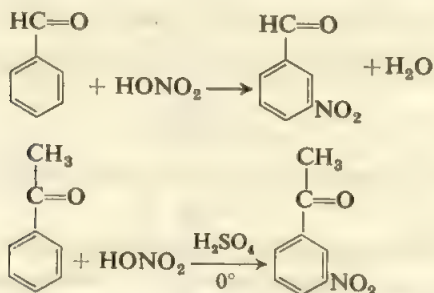
Cleavage then yields iodoform:



Isopropyl alcohol and all other secondary 2-alkanols oxidize to methyl ketones and consequently give a positive iodoform test.

#### D. RING SUBSTITUTION REACTIONS

Aromatic aldehydes and ketones have the potentiality for undergoing substitution in the aromatic ring. Sulfonation, halogenation and nitration lead to ring substitution mainly in the *meta* position. The equation for a typical substitution reaction of benzaldehyde and of acetophenone is as follows:

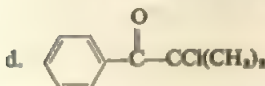
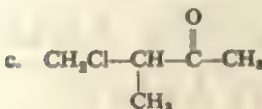
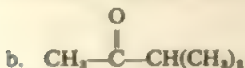


It should be noted that the aldehyde group is particularly sensitive to oxidation by nitric acid and halogens and for best yields should be protected when substitution reactions using these reagents are attempted.

#### EXERCISES

1. What group of atoms is responsible for the chemical properties of: (a) alkenes, (b) alcohols, (c) aldehydes, (d) ketones?
2. Define: (a) functional group, (b) polar bond, (c) addition reaction, (d) electrophilic, (e) oxidation, (f) mixed ketone, (g) an aldol, (h) an  $\alpha$ -hydrogen.
3. Name, using both common names and IUPAC names, and write the structural formulas for 3 common aldehydes and 3 common ketones.

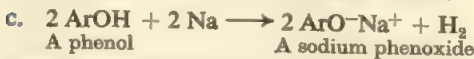
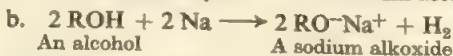
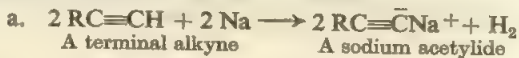
4. Use these endings correctly in IUPAC names of compounds: (a) *ene*, (b) *ane*, (c) *yne*, (d) *one*, (e) *al*.
5. Name each of these compounds correctly by the IUPAC system.



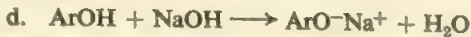
6. Write equations showing any catalysts or special conditions for the two-step preparation of:
- benzaldehyde (phenyl methanal) from toluene
  - acetaldehyde from ethyl chloride
  - formaldehyde from carbon monoxide, hydrogen and oxygen
  - acetaldehyde from calcium carbide and water
7. Write equations for the additions of four different reagents to a carbonyl compound.
8. Write an equation for an aldol condensation.
9. Which of these compounds: (a) form a silver mirror with Tollens' reagent, (b) form a red precipitate with Fehling's solution, (c) decolorize cold basic potassium permanganate solution, (d) form iodoform when added to an aqueous solution of iodine and sodium hydroxide: (i) ethanol, (ii) isopropyl alcohol, (iii) propane, (iv) propene, (v) formaldehyde, (vi) benzaldehyde, (vii) methyl ethyl ketone?

# ORGANIC ACIDS AND THEIR DERIVATIVES

Some compounds which are acids according to the Brönsted-Lowry definition have already been encountered among the organic compounds studied. Protons are donated by terminal alkynes, alcohols and phenols upon reaction with sodium.



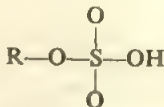
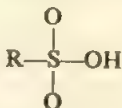
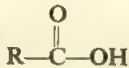
Of these three classes of compounds, only phenols are sufficiently acidic to react with a strong base in aqueous solution. Phenols alone are more acidic than water:



The acids to be discussed in this chapter, like phenols, are more acidic than water and may therefore be neutralized by bases in aqueous solution.

## 1. ORGANIC ACIDS

Among the various organic acids are the carboxylic acids, the sulfonic acids, the alkyl hydrogen sulfates, the thiocarboxylic acids and the alkyl phosphonic acids. Three of these acids are shown in Figure 34.1.



## Carboxylic acids

## Sulfonic acids

### Alkyl hydrogen sulfates

**Figure 34.1. Types of organic acids.**



The three most important types of organic acids (Fig. 34.1) are hydroxy

acids, as are sulfuric acid ( $\text{HO}-\overset{\text{O}}{\underset{\text{O}}{\text{S}}}-\text{OH}$ ) and nitric acid ( $\text{HO}-\overset{\text{O}}{\text{N}}-\text{O}$ ). The

hydrogen of a hydroxyl group is the active hydrogen, the one lost as a proton upon reaction with a base. In each acid the acidic hydroxyl group is attached to a non-metal. In each acid there is more than one equivalent position for the hydrogen. This can be illustrated by showing the anions obtained when the proton is lost from sulfuric acid, methanesulfonic acid and ethyl hydrogen sulfate (Fig. 34.2).

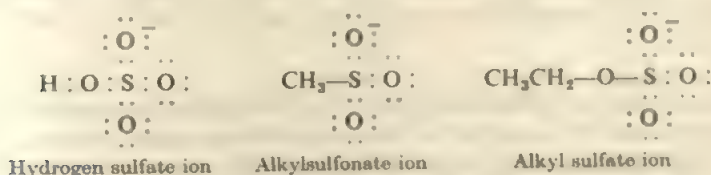


Figure 34.2. Anions of acids.

The two equivalent positions for reception of a proton by the carboxylate ion (the anion of carboxylic acids) are not apparent in the customary formula (Fig. 34.3a). The formula is inadequate.

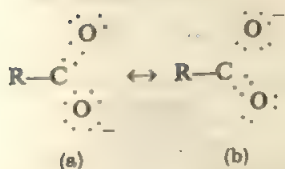


Figure 34.3. The carboxylate ion.

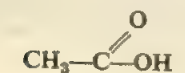
It is sometimes said that there is *resonance* between the structures shown in Figure 34.3a and b. This means that neither is the correct structure, but that the correct structure is something intermediate between the two. Figure 34.3c is a better representation. Between carbon and each oxygen is a sigma bond. A delocalized bond contains the other two electrons in an orbital about the three atoms: carbon and both oxygens.

This chapter will discuss carboxylic acids (by far the most important organic acids) and derivatives of carboxylic acids. Industrial sulfonic acids will be mentioned when deemed advisable.

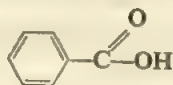
## 2. NOMENCLATURE

Carboxylic acids may contain one or more carboxyl groups. The number of groups may be designated by the prefixes *mono-*, *di-*, and *tri-*. Acetic acid,

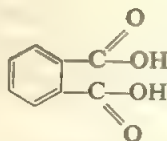
$\text{CH}_3-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{OH}$ , is a monocarboxylic acid. The carboxyl group may be either the end carbon of a chain or may be attached to an aromatic carbon. They are called aliphatic and aromatic carboxylic acids, respectively. Some acids are shown in Figure 34.4.



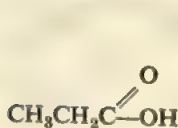
Acetic acid  
(an aliphatic acid)



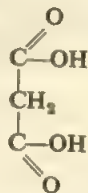
Benzoic acid  
(an aromatic acid)



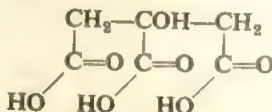
*o*-Phthalic acid  
(a benzene dicarboxylic acid)



Propionic acid  
(an aliphatic acid)



Malonic acid  
(an aliphatic di-carboxylic acid)



Citric acid  
(an aliphatic tri-carboxylic acid)

Figure 34.4. Some carboxylic acids.

When animal fats are boiled in lye (sodium hydroxide solution) and then acidified, many monocarboxylic acids containing from 6 to 22 carbons precipitate from the solution. Most of the R-groups of the acids obtained are unbranched alkane chains. For this reason, *saturated monocarboxylic acids are called fatty acids*. Some long chain unsaturated acids (acids having one or more double carbon to carbon bonds) appear with them. These are called *unsaturated fatty acids*.

Common names are used widely for carboxylic acids. Names of the first ten members of the normal fatty acid series appear with others in Table 34.1.

**Table 34.1. Physical Properties of Some Acids**

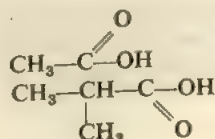
No. of Carbons	Common Name	Melting Point °C	Boiling Point °C	Solubility in Water g/100 g Water	IUPAC Name
1	Formic*	8.3	101	Completely	Methanoic Acid
2	Acetic	16.67	119	Completely	Ethanoic Acid
3	Propionic	-36.0	141	Completely	Propanoic Acid
4	Butyric†	-4.7	163	5.62	Butanoic Acid
5	Valeric	-34.5	186	3.7	Pentanoic Acid
6	Caproic	-1.5	205	0.4	Hexanoic Acid
7	Heptylic	-10.5	223	—	Heptanoic Acid
8	Caprylic	16.5	237	0.25	Octanoic Acid
9	Pelargonic	12.5	254	—	Nonanoic Acid
10	Capric	31.4	269	Slightly	Decanoic Acid
16	Palmitic	63.1	268	Insoluble	Hexadecanoic Acid
18	Stearic	70.1	287	Insoluble	Octadecanoic Acid
18	Oleic	13.5	—	Insoluble	9-Octadecenoic Acid
7	Benzoic	121.0	250	0.18	Benzene-carboxylic Acid
9	Phthalic	213.0	—	0.54	1,2-Benzene-dicarboxylic Acid
2	Oxalic	101.2	Subl. 150	9.5	Ethandioic Acid
3	Malonic	135.6	Decomposes	73.5	Propanedioic Acid
6	Adipic	152.0	265	1.5	Hexanedioic Acid

\* From *formica*, the Latin word for ants; it was first prepared by distillation of red ants.

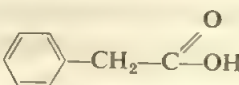
† Found in rancid butter.

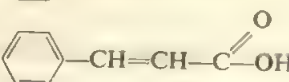
Systematic IUPAC names for monocarboxylic acids are obtained by changing the ending *e* of the name of the parent hydrocarbon with the suffix *oic*, followed by the word *acid*. The carbon of the carboxyl group must be one of the chain and must be number *one*. It need not be numbered in the name. Branches and groups are named and placed by number as usual, for example:

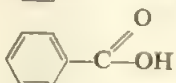
Acetic acid  
Isobutyric acid



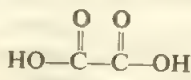
is ethanoic acid.  
is 2-methylpropanoic acid.

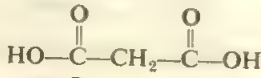
Phenyl acetic acid  is 2-phenylethanoic acid.

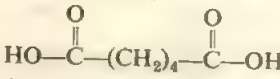
Cinnamic acid  is 3-phenyl-2-propenoic acid.

Benzoic acid  is phenylmethanoic acid.

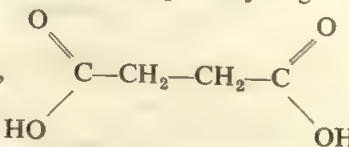
Dicarboxylic acids have the suffix *dioic*:

Oxalic acid  is ethandioic acid.

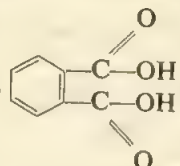
Malonic acid  is propandioic acid.

Adipic acid  is hexandioic acid.

Acceptable systematic names may be assigned by appending the name "carboxylic acid," "dicarboxylic acid," etc., to the name of the compound in which the carboxyl groups replace hydrogens. For example, succinic (or

butandioic\*) acid, , may be called ethane-

1,2-dicarboxylic acid. These names are especially useful for aromatic acids.

o-Phthalic acid, , may be called benzene 1,2-dicarboxylic acid.

### 3. PHYSICAL PROPERTIES

Physical properties of some carboxylic acids are listed in Table 34.1. There are no carboxylic acid gases at room temperature. The smaller members of the monocarboxylic acid series are soluble (up to 4 carbons). Dicarboxylic acids are solids and are about as soluble as monocarboxylic acids of the same molecular weight. This one might expect, knowing the geometry and hence the polarity of the carboxyl group. The acids are more soluble in strongly basic solutions than in water. This is due to the reaction with the base (neutralization) to form ionic compounds.

Smaller members of the monocarboxylic acid series have a sour taste and a biting odor. The odor of the second member, acetic acid, is well known. At butyric acid (4 carbons), the acrid odor is replaced by disagreeable odors.

\* IUPAC name.



The disagreeable odor of sour milk and rancid butter is due largely to normal butyric acid. Caproic acid (hexanoic acid) is present in the skin and in secretions of goats. It is responsible for the "goaty" odor. Longer chain fatty acids, being much less volatile, are practically odorless.

#### 4. PREPARATION OF CARBOXYLIC ACIDS

Carboxylic acids may be prepared by a variety of methods, most of which involve oxidation or hydrolysis of suitable compounds.

##### A. OXIDATION

The various oxidation reactions giving carboxylic acids as products have been discussed as reactions of other compounds. Types of compounds that may be oxidized to acids are:

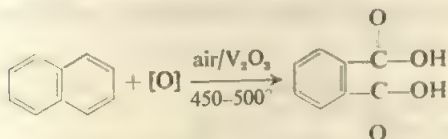
(1) *Unsaturated hydrocarbons.* Cleavage occurs at the multiple bond, yielding two acids unless the compound is symmetrical or unless the multiple bond is terminal (Chapter 30).

(2) *Primary alcohols* can be oxidized, first to aldehydes, then to carboxylic acids (Chapter 32).

(3) *Aldehydes* are oxidized to acids (Chapter 33).

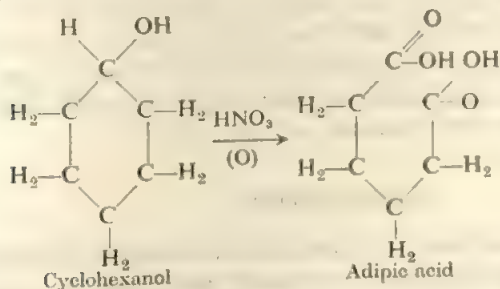
(4) *Side chains of aromatic compounds* are oxidized readily to acids (Chapter 31).

An interesting oxidation of benzene side chains is that of naphthalene:



The second ring is oxidized as if it were two side chains.

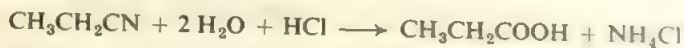
The oxidation of the specific secondary alcohol, cyclohexanol, is also of interest:



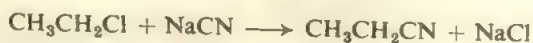
This is an intermediate reaction in the preparation of nylon. Phenol from coal tar is hydrogenated to cyclohexanol, which is oxidized by nitric acid (as shown above) to give one of the two reactants which, when combined, give the polymer.

## B. HYDROLYSIS

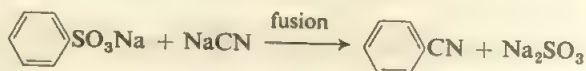
(1) *Hydrolysis of nitriles* (cyanides) and the various types of acid derivatives yields carboxylic acids. Both alkyl and aryl carboxylic acids can be obtained in this way. For example, propionitrile yields propionic acid, and benzonitrile yields benzoic acid,



Alkyl nitriles are readily formed from alkyl halides by the reaction:

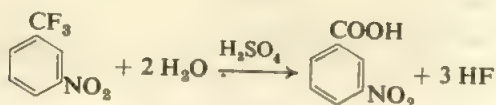


This conversion makes it possible to use alkyl halides as starting materials for preparing carboxylic acids. Aryl nitriles, on the other hand, may be prepared from the sodium or potassium salts of aromatic sulfonic acids upon fusion with sodium cyanide.



Since aromatic sulfonic acids are readily prepared by sulfonation, this reaction serves as one step in the pathway to aromatic carboxylic acids from aromatic hydrocarbons themselves.

(2) *Trihalomethyl groups are readily hydrolyzed to carboxyl groups.* This method serves as the most suitable means for obtaining some particular carboxylic acids.



Of great practical importance are the hydrolysis reactions of the various acid derivatives. These reactions will be discussed in later sections of this chapter. Many carboxylic acids are obtained by the hydrolysis of naturally occurring esters, such as the fats, oils or waxes. Esters of this class are to be discussed in the next chapter. The hydrolysis of proteins, amides found in all living matter, is the principle source of many amino carboxylic acids. Proteins and amino acids will be discussed in Chapter 38.

## 5. REACTIONS

The characteristic reactions of the carboxylic acids are due to the presence of the carboxyl functional group. Structurally the group is a composite of a carbonyl group and a hydroxyl group, a fact more clearly shown when

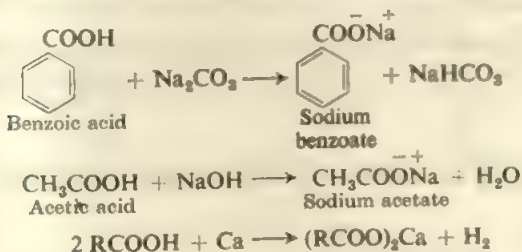
its structure is expanded and written as  $\text{—}\overset{\text{O}}{\underset{\parallel}{\text{C}}}\text{—OH}$ .

Although the reactions which such acids might be expected to show would be those of both the carbonyl and the hydroxyl groups (studied in the two previous chapters), when combined as they are here, they do not exhibit the properties that might be expected. The hydroxyl influence decreases the reactivity (polarity) of the carbonyl group to such an extent that acids behave very little like aldehydes or ketones. Some reactions of carboxylic acids, however, are similar to those of alcohols. The more characteristic reaction of the carboxylic acids is that of neutralization, or salt formation. The hydrogen of the hydroxyl group is weakly acid for reasons explained previously in this chapter. All carboxylic acids are nearly the same strength as acetic acid, whose ionization constant is  $1.8 \times 10^{-5}$ .

Familiar acids (proton donors), when compared with carboxylic acids with respect to decreasing strength as acids, fall in the general pattern:  $\text{HCl} > \text{RSO}_2\text{OH} > \text{RCOOH} > \text{C}_6\text{H}_5\text{OH} > \text{HOH} > \text{ROH} > \text{RC}\equiv\text{CH} > \text{NH}_3$ .

#### A. REPLACEMENT OF THE HYDROGEN OF THE CARBOXYL GROUP. SALT FORMATION

Since the carboxyl  $-\text{OH}$  loses a proton much more readily than does the  $-\text{OH}$  of alcohols, corresponding reactions associated with the replacement of the hydrogen of the carboxyl occur more readily. These acids react with active metals and with a variety of bases, such as sodium hydroxide or sodium carbonate, to form salts. Equations for typical reactions are:

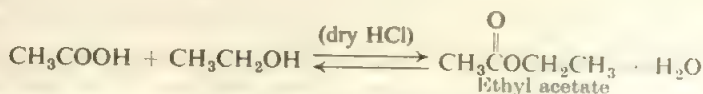


Acetic acid forms soluble salts with almost all metals. Salts of larger acids are less soluble. The metal salts (particularly the sodium and potassium salts) of the long chain fatty acids, such as palmitic and stearic acids, are known as soaps. They will be discussed with the fats and oils.

#### B. REPLACEMENT OF THE HYDROXYL OF THE CARBOXYL GROUP

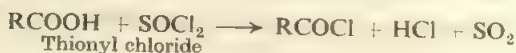
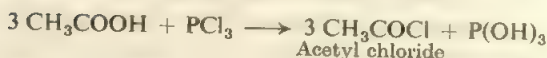
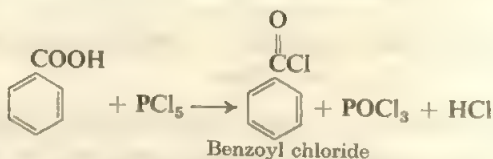
A variety of reagents react with carboxylic acids to exchange the  $-\text{OH}$  with other groups. Compounds derived from the carboxylic acids by substituting an atom or group for the  $-\text{OH}$  are known as acid derivatives. Typical compounds formed by replacing the carboxyl  $-\text{OH}$  include the acid halides, acid anhydrides, acid amides and esters. These will be discussed briefly here. Further treatment will be given them later in the chapter.

(1) *Alcohols react with carboxylic acids to form esters.* The classical reaction which illustrates this transformation is that of acetic acid with ethyl alcohol:



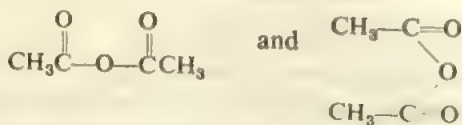
To achieve this, a strong acid, such as sulfuric acid or dry hydrogen chloride gas, is usually employed as a catalyst for the reaction. An examination of the structure written for the ester shows that the —OH has been replaced with an alkoxy group (—OR).

(2) *Carboxylic acids react with phosphorus halides or thionyl chloride (SOCl<sub>2</sub>) to form acid halides*, also referred to as acyl halides. The acid chlorides are more often prepared than other acid halides. For this reason the equations for the reactions to illustrate this phenomenon are written for the formation of the chlorine compounds.

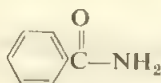


(3) *Acid anhydrides are not usually prepared directly from acids*, although structurally they are compounds in which the —OH of the carboxyl group is

replaced with an acyl ( $\text{RC}(=\text{O})$ ) group. Alternate formulas for acetic acid anhydride are:



(4) *Likewise acid amides, acid derivatives in which the —OH of the carboxyl is replaced with an —NH<sub>2</sub> group*, which would appear to be readily obtainable directly from the acid, are better prepared by other procedures. The formula for benzamide (benzoic acid amide), derived from benzoic acid, is:

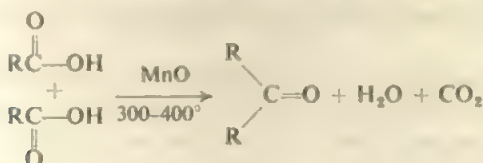


### C. DECARBOXYLATION

Decarboxylation refers to the transformation which removes the carboxyl group of an acid. Direct decarboxylation can be conveniently accomplished



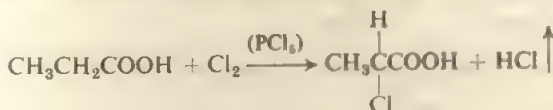
by passing the acid through a hot tube packed with  $\text{MnO}$  as a catalyst. The equation for the reaction is:



More often decarboxylation is achieved by heating the sodium salt of the acid with soda-lime, a mixture of  $\text{NaOH}$  and  $\text{CaO}$ .

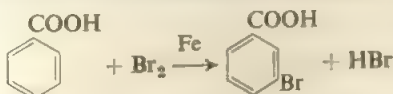
#### D. SUBSTITUTION OF ALPHA HYDROGENS

Because the highly polar carboxyl group strongly attracts the electrons of the carbon to which it is attached, the hydrogens joined to this alpha-carbon are rather easily substituted. These alpha hydrogens may be displaced by halogens in the presence of a suitable catalyst.



#### E. AROMATIC SUBSTITUTION REACTIONS

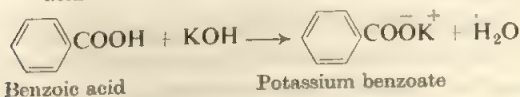
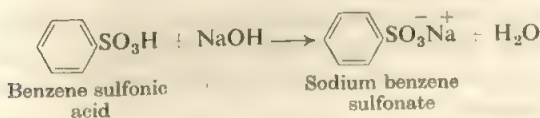
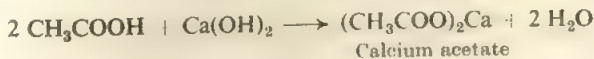
Aromatic acids undergo the usual aromatic substitution reactions. The *carboxyl group is deactivating and meta-directing*. Bromination of benzoic acid yields meta-bromobenzoic acid by a reaction that is more difficult to achieve than the bromination of benzene.



### 6. ACID DERIVATIVES

#### A. SALTS

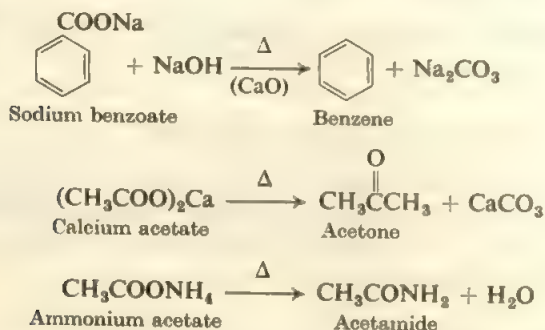
Salts are ionic compounds formed by the reaction of organic acids with bases:



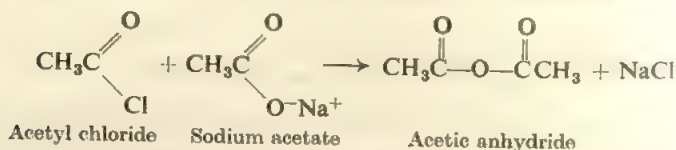
To form the name of a salt from the acid requires two operations. First,

change the *ic* ending of the name of the acid to *ate*, and then place the name of the metal in front of the term obtained. By this procedure the sodium salt of formic acid becomes sodium formate; the potassium salt of stearic acid, potassium stearate.

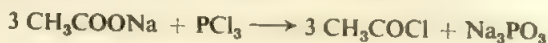
Particular salts of organic acids undergo characteristic thermal decompositions (decarboxylation or dehydration) which, depending on the type of salt, yield hydrocarbons, ketones, aldehydes or, with ammonium salts, amides.



Acid anhydrides are formed when salts react with acid halides:

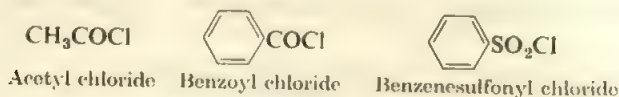


Salts also react with phosphorus halides ( $\text{PCl}_3$ ), much as do the free acids, to form acid chlorides, an industrially useful reaction because the salts are obtained more cheaply than acids:



### B. ACID HALIDES

Acid halides are formed from organic acids by replacing the  $-\text{OH}$  of the acid group with a halogen atom:



The more important acid chlorides will be employed to illustrate the preparations and the chemical transformations which such substances undergo. Acid bromides and iodides, when obtained, exhibit essentially the same reactions as do the chlorides.

Common names of acid halides are formed by first replacing the *ic* ending of the name used for the acid with *yl*, forming a name to which one adds the name chloride, bromide or iodide. The acid chloride prepared from acetic acid is *acetyl chloride*. The acid chloride formed from benzene sulfonic acid

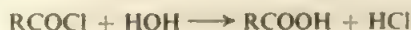
becomes benzene sulfonyl chloride; the acid bromide of propionic acid, propionyl bromide.

Acid chlorides are readily prepared from either the acids or their salts. Acids react with phosphorus chlorides ( $\text{PCl}_3$ ,  $\text{PCl}_5$ ) or thionyl chloride ( $\text{SOCl}_2$ ) to produce acid chlorides (see p. 564). Sodium salts also react with phosphorus trichloride ( $\text{PCl}_3$ ) in much the same manner as acids to form acid chlorides (see p. 566). It should be noted that these preparatory reactions were previously studied as reactions of acids.

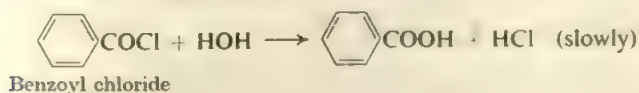
Acid halides react with many compounds having reactive hydrogen atoms

O  
||

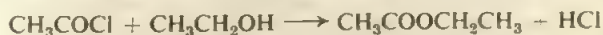
to introduce an  $\text{RC—}$  group (acyl group) in place of a hydrogen atom. The great activity of acid chlorides makes them excellent synthetic reagents. The smaller acid chlorides (acyl chlorides) of the aliphatic series react violently with water or vapor in the air to form the free acid. They are lacrymators and irritate both the eyes and throat. This reaction is referred to as hydrolysis:



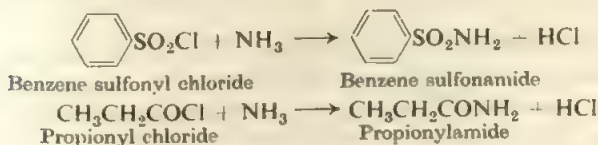
The higher members of this nonaromatic series react less rapidly, due to their decreasing solubility in water. The chlorides of aromatic acids are inherently more resistant to hydrolysis and are usually hydrolyzed only very slowly by cold water, but more rapidly with hot.



A similar reaction with an alcohol is referred to as *alcoholysis* and the product formed is an ester. This is a good method for preparing esters:



The corresponding reaction with ammonia is known as *ammonolysis*. The compound obtained is an amide. This reaction is an excellent method for preparing amides.

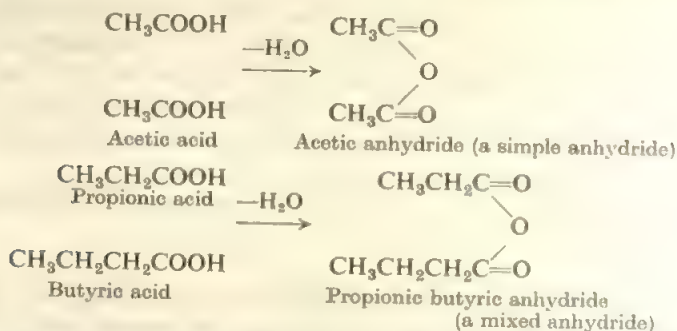


Since in each of the above transformations the acyl ( $\text{RCO—}$ ) group is introduced, such reactions are commonly referred to as *acylation* reactions.

### C. ACID ANHYDRIDES

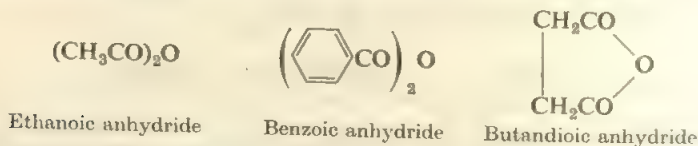
Structurally an acid anhydride may be regarded as the product obtained when a molecule of water is removed from two molecules of acid. If the water is removed from two molecules of the same acid, a simple anhydride is

obtained. The anhydride formed from two different acids is known as a mixed anhydride:

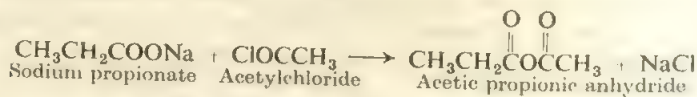


The common names of acids are used to form the common names of the anhydrides. The term acid is dropped and replaced with the term anhydride in naming simple anhydrides. To name a mixed anhydride, the stem names of the two different acids are given, followed by the term anhydride.

The systematic IUPAC names are formed in a similar manner from the systematic names of the parent acids. For example, acetic anhydride becomes ethanoic anhydride; succinic anhydride, butandioic anhydride.

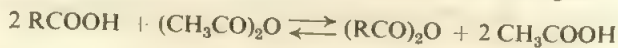


Although the formulation which shows the splitting out of water implies that anhydrides are formed directly from acids by dehydration, in actual practice the preparation of an acid anhydride is not that simple. The classical method (p. 566) for preparing them is the reaction of an acid halide with the sodium salt of an acid.



This reaction is particularly useful for preparing mixed anhydrides.

Anhydrides of acids may also be prepared by refluxing the acid with acetic anhydride or acetyl chloride. The acetic anhydride and chloride serve as dehydrating agents. This reaction is not a simple dehydration. The easy removal of acetic acid shifts the equilibrium far to the right:

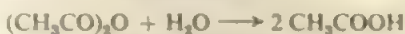


Anhydrides are analogous in their behavior to acid halides and show the type of reactions which were discussed in the previous section for acid chlorides. However, they are considerably less reactive.

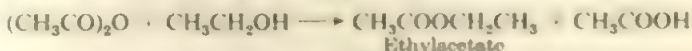
Anhydrides undergo hydrolysis. The reaction of acetic anhydride with water is rather slow compared to that of acetyl chloride. For the higher



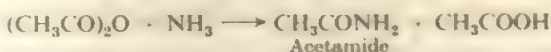
anhydrides, it is often necessary to boil them with water for some time before they are completely hydrolyzed.



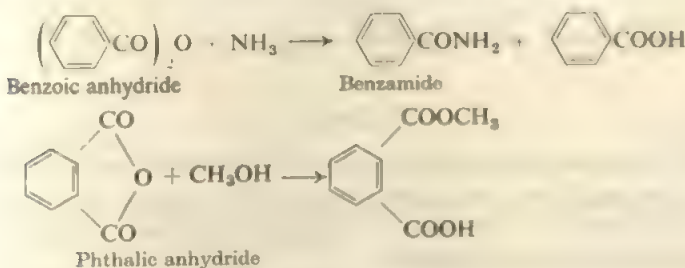
Alcoholysis leads to the formation of esters in a transformation entirely analogous to that discussed for acid chlorides:



Ammonolysis forms the corresponding amide:

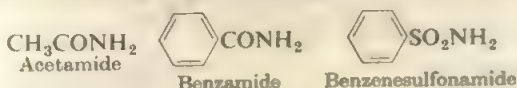


Similar reactions occur with aromatic anhydrides and with the cyclic anhydrides of dibasic acids, such as succinic and o-phthalic acids:

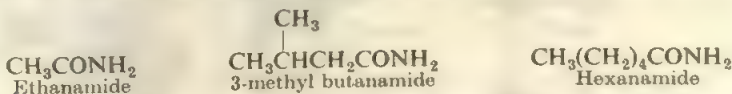


#### D. AMIDES

Amides of carboxylic acids have the general formula,  $\text{RCONH}_2$ ; those of sulfonic acids,  $\text{RSO}_2\text{NH}_2$ . Typical compounds of this class are -

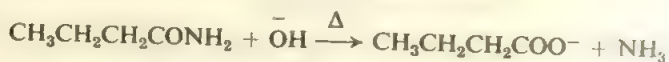


Common names are used most frequently for these compounds. The common names are formed by replacing the ending "ic acid" from the common name of the acid with "amide." The IUPAC systematic names are formed in the usual way. The names for amides of aliphatic carboxylic acids are obtained by replacing the terminal "e" of the systematic name of the alkane having the same number of carbon atoms with the term "amide." Any substituents are designated by name and located by number with the carbon of the amide group numbered as carbon 1.

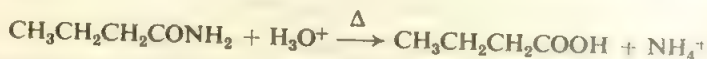


In previous sections of this chapter, reactions by means of which amides can be prepared have been discussed. These include their formation from ammonium salts (p. 566), from acid chlorides (p. 567) and acid anhydrides (p. 569). They may also be prepared as a result of the reaction of esters with ammonia (p. 572).

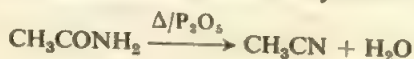
Amides undergo hydrolysis, as do the other acid derivatives. They react extremely slowly with water alone, but they do hydrolyze when heated under reflux with excess aqueous alkali. The course of the reaction may be followed by the evolution of ammonia. Alcoholic potassium hydroxide may be used for the hydrolysis of some less soluble compounds:



Aqueous mineral acids act similarly:

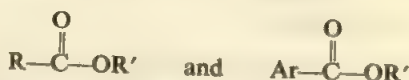


Dehydration of amides leads to the formation of nitriles, whose characteristic structural feature is the presence of a  $\text{—CN}$  group. Compounds having this group are referred to as nitriles or cyanides.



### E. ESTERS

Esters are formed when alcohols react with acids to split out a molecule of water. Structurally they are derived from acids by replacing the  $\text{—OH}$  group of the acid group with an alkoxy ( $\text{—OR}$ ) group and accordingly they are represented by the general formulas:



Three dimensional models which show more clearly the structure of two of the simplest esters are given in Figure 34.5.

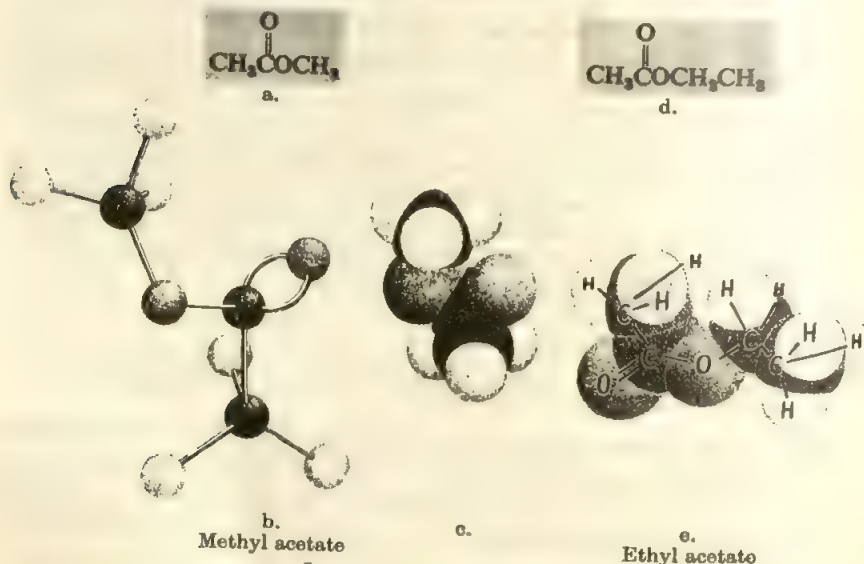
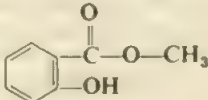
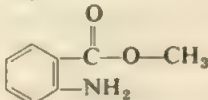


Figure 34.5. Simple esters.

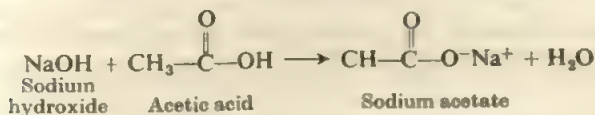
Esters are compounds of great importance. They are widely distributed in nature. The active ingredient responsible for the pleasant flavor and odor of a fruit or flower is often an ester.

Some esters and their pleasant odors are listed below:

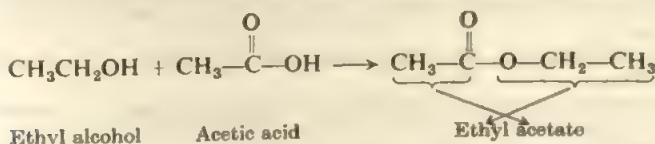
Amyl acetate (1-pentylacetate)	$\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-(\text{CH}_2)_4-\text{CH}_3$	banana odor
Octyl acetate	$\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-(\text{CH}_2)_7-\text{CH}_3$	orange odor
Ethylbutyrate	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{CH}_2-\text{CH}_3$	pineapple odor
Methyl salicylate		oil of wintergreen
Methyl anthranilate		intense odor of grape

Animal and vegetable fats and oils are esters. They will be discussed more completely in the following chapter.

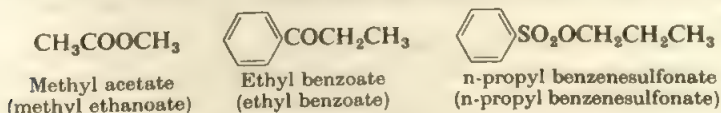
Esters were once thought to be salts of organic acids and therefore the common names are similar to the common names for salts. For example, the salt of sodium hydroxide and acetic acid is sodium acetate:



Similarly the ester of ethyl alcohol and acetic acid is ethyl acetate.



The common and most used name of an ester contains the alkyl group of the alcohol followed by the name of the acid with the suffix changed from *ic* to *ate*. By this procedure, the methyl ester of acetic acid becomes *methyl acetate*; the ethyl ester of benzoic acid becomes *ethyl benzoate*.

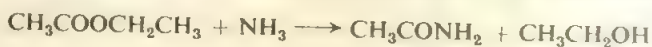


The IUPAC names are similar. However, the systematic names of the acids and alcohols, and not their common names, are used. For example, methyl

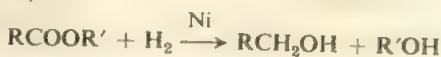
acetate is also named *methyl ethanoate*; ethyl butyrate becomes *ethyl butanoate*.

The formation of an ester by direct reaction of an alcohol with an acid is referred to as *esterification*. This is usually effected by warming a solution of the acid in an excess of the appropriate alcohol, using as a catalyst either a little sulfuric acid, or gaseous hydrogen chloride bubbled into the alcohol-acid mixture. The homologs of formic acid, the aromatic acids and many hydroxy acids, as well as dibasic acids, can be converted into esters by this method (p. 564). Other, and often better, methods include the reaction of an alcohol with an acid chloride (p. 567) or with acetic anhydride (p. 569).

As typical acid derivatives, esters may undergo hydrolysis. This may be carried out with basic or acidic catalysts. Basic hydrolysis is referred to as saponification. This reaction is widely used to make soaps from fats and oils. Esters also undergo ammonolysis to form amides; the reaction is:



Esters may also be converted to alcohols by catalytic hydrogenation (reduction):



This reaction is important in the preparation of long chain alcohols from naturally occurring fats and oils in the industrial manufacture of synthetic detergents.

## EXERCISES

- List in the order of increasing acidity: water, phenol, ammonia, alcohol, sulfuric acid, sulfonic acids, carboxylic acids and alcohols.
- What substances and solutions might one use to test the acidity of an unknown organic compound?
- Define each term and name and write the structural formula for an example of each: (a) fatty acid, (b) diprotic (dibasic) carboxylic acid, (c) tribasic acid, (d) an aromatic acid, (e) a sulfonic acid, (f) an alkyl hydrogen sulfate, (g) an acid halide, (h) an acid anhydride, (i) an ester.
- Define: (a) resonance, (b) relative acidity, (c) displacement, (d) replacement, (e) substitution.
- Explain why the hydrogen of the carboxyl group should be acidic. Correlate the discussion with the acidic nature of the hydrogens in sulfuric acid.
- Write equations for a one-step preparation of an acid from each substance listed, showing any catalysts and special reaction conditions required: (a) ethyl benzene, (b) 2-butene, (c) ethyl acetate, (d) acetaldehyde, (e) isobutyl alcohol, (f) ethyl cyanide, (g) 1,1,1-triiodohexane.
- Write equations showing all catalysts and/or special conditions illustrating: (a) decarboxylation, (b) salt formation, (c) esterification, (d) hydrolysis, (e) alcoholysis, (f) ammonolysis, (g) halogenation of an  $\alpha$ -hydrogen of an acid, (h) acid chloride formation.
- Write reactions for and compare the ease of reactions of acids, acid chlorides, amides, acid anhydrides and esters with: (a) water, (b) ammonia, (c) solution of NaOH, (d) alcohols.
- Write equations for each step of this synthesis:
  - 1-butyne is heated with basic potassium permanganate
  - the liquid product is treated with thionyl chloride
  - the reactive product formed is added to isopropyl alcohol



## FATS AND OILS

The organic matter of living cells is made up largely of three types of substances: lipids, carbohydrates and proteins. Lipids are a rather heterogeneous collection of substances obtained by the exhaustive extraction of biological materials with those liquids commonly referred to as "fat solvents" (i.e., methanol, ethanol, acetone, chloroform, carbon disulfide, ether or benzene). Among the substances that are soluble in these organic solvents are *fats* and *oils*, cerebrosides (in the brain), sphingomyelins (nerve tissue), lecithins and cephalins (phosphorus-containing compounds) and cholesterol (found in the blood). All are important in the chemistry of living organisms. Fats and oils comprise the bulk of the lipids.

## 1. COMPOSITION OF FATS AND OILS

The naturally occurring fats and oils—lard, beef tallow, whale blubber, cottonseed oil, palm oil, olive oil, corn oil, etc.—are lipids, which are insoluble in water, but which may be hydrolyzed in hot sodium hydroxide solution to give glycerol and sodium salts of long chain fatty acids called soaps.

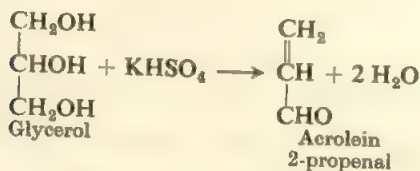
## A. GLYCEROL

Glycerol (1,2,3-propantriol) is completely soluble in water, has a sweet taste and is non-toxic. It is used widely in medicines, cosmetics and foods. Glycerol is hygroscopic, that is, it absorbs water vapor from the atmosphere. For this reason it is used as a humectant in non-drying inks and tobacco.

Glycerol is an antifreeze. The trihydroxy alcohol (glycerol) reacts with nitric acid to form nitroglycerin, the active constituent of dynamite (p. 530).

The amount of glycerol obtained as a by-product in soap manufacture cannot meet great demands for dynamite, as, for example, during wartime. Additional glycerine may be made by fermentation of sugar or from propylene, a cracking by-product in the petroleum industry. Today, large quantities of glycerol are made from propylene.

When glycerol is heated to a high temperature it is dehydrated to acrolein. In the presence of potassium hydrogen sulfate, the reaction takes place at a lower temperature.



Acrolein has a very irritating odor. It may be detected in the fumes resulting from burning animal or vegetable fats.

### B. FATTY ACIDS

When the hydrolysis mixture (resulting from the hydrolysis of a fat or an oil in a basic solution) is acidified, the acid salts are converted into an oily, insoluble mixture of carboxylic acids. Repeated analysis of the resulting acids have shown them to be mostly *long chain* acids with an *even number* of carbons. The acid chain *may* or *may not* contain *double bonds*. Only very small amounts of fatty acids with either an odd number of carbon atoms or with branched carbon chains have been found and these have come from very special sources. For example, isovaleric acid (3-methylbutanoic acid), having both an uneven number of carbons and a methyl branch, is found in dolphin and porpoise blubber.

Some of the saturated fatty acids commonly found in natural fats or oils are listed in Table 35.1. The two most commonly occurring are palmitic acid (16 carbons) and stearic acid (18 carbons), with palmitic acid generally the more abundant.

Table 35.2 lists several important unsaturated fatty acids which are found in many fats and oils. It is apparent that oleic acid is the one most widely distributed in nature.

### C. FATS AND OILS

From a consideration of their hydrolysis products, which are an alcohol and the sodium salts of acids, one must assume that *fats and oils are esters*. Analyses show that three molecules of acid are liberated in the hydrolysis for each molecule of glycerol. Reconstructing the substance, a triester of

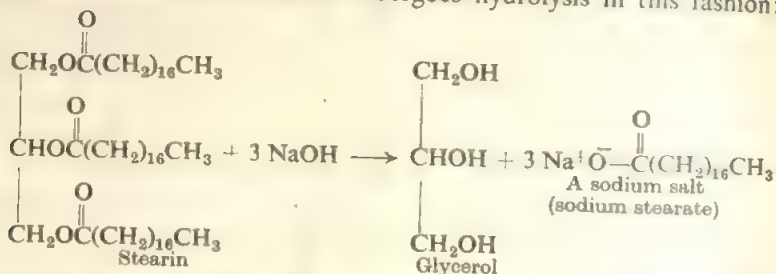
Table 35.1. Saturated Acids Commonly Found in Natural Fats and Oils

Name	Formula	Percentage in			
		Butterfat	Cottonseed Oil	Lard	Human
Myristic acid	$\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$	12	1	2	2.7
Palmitic acid	$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$	25	22	29	24
Stearic acid	$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$	9	2	14	8.4
Arachidonic acid	$\text{CH}_3(\text{CH}_2)_{18}\text{COOH}$	1	2	—	1

Table 35.2. Unsaturated Acids Commonly Found in Natural Fats and Oils

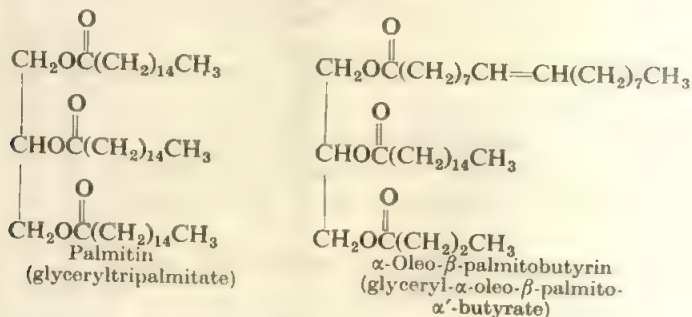
Name	Formula	Percentage in			
		Butterfat	Cottonseed Oil	Lard	Human
Palmitoleic acid	$\text{CH}_3(\text{CH}_2)_5\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	5	1	2	5
Oleic acid	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	35	28	45	47
Linoleic acid	$\text{CH}_3(\text{CH}_2)_2\text{CH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	5	44	6	10.2
Linolenic acid	$\text{CH}_3(\text{CH}_2)_3\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	5	—	—	1.5

glycerol is determined. The triester undergoes hydrolysis in this fashion:



Stearin, the fat molecule used above to illustrate the hydrolysis of an ester, is a simple triester of glycerol, a simple *triglyceride*. All three acid groups are identical. The salt of only one acid is found among the hydrolysis products. A *mixed triglyceride* is one in which there are two or three different acid groups.

Common names of simple triglycerides are formed by first naming the acid esterified with the glycerol, then dropping the ending *ic* of the name of the acid and adding the ending *in*. The triglyceride formed from palmitic acid is palmitin; from stearic acid, stearin; and from oleic acid, olein. The names of the mixed triglycerides are obtained by naming the individual acids without endings, except for the last named, and then designating their location by the Greek symbols  $\alpha$ ,  $\beta$  and  $\alpha'$ . The terminal positions of glycerol are designated by the  $\alpha$  and  $\alpha'$ . The central carbon of glycerol is specified by  $\beta$ . Esters of glycerol may also be named as simple esters. The names derived in this way are given in the parentheses.



Both simple and mixed triglycerides may be present in natural fats and oils. For the most part, however, they consist of a rather complicated mixture of glycerides, almost exclusively of the mixed type. Simple glycerides occur very infrequently unless one of the fatty acids happens to be present in particularly large amounts (50% or more).

## 2. PHYSICAL PROPERTIES OF FATS AND OILS

Structurally, the fats and oils are compounds of the same type, and are distinguished from each other on the basis of their physical state at ordinary temperatures. Fats are solids and oils are liquids. It should be apparent that



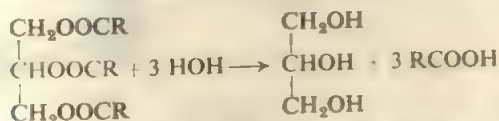
the distinction is often rather vague since the physical state in a particular locality depends upon the climate, weather and other not too clearly defined variables.

The physical properties of a particular fat or oil are an expression of its fatty acid composition. Correspondingly, other factors being the same, a fat or oil with a larger percentage of shorter chain (lower molecular weight) fatty acids will exhibit greater water solubility and a lower melting point than other fats with a lesser percentage. Likewise, glycerides containing larger amounts of unsaturated fatty acids will generally exhibit lower melting points than similar glycerides containing smaller quantities. Thus, if two glycerides containing the same number of carbon atoms, one of which is solid and the other liquid, are compared, the liquid glyceride invariably contains the higher percentage of unsaturated acid. Oils (liquid fats) are usually characterized by a higher content of unsaturated fatty acid groups than solid fats.

### 3. CHEMICAL PROPERTIES: REACTIONS AND PRODUCTS

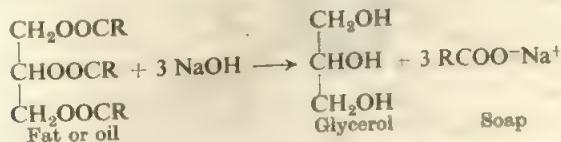
#### A. HYDROLYSIS

Probably the most important chemical reaction of fats and oils is that of *hydrolysis to form fatty acids and glycerol*. Three molecules of fatty acid and one molecule of glycerol are formed per molecule of fat or oil hydrolyzed.



Since this reaction takes place only very slowly in boiling water, various catalysts have been employed to increase the rate at which the transformation proceeds. Both acids and bases catalyze the reaction, as do certain digestive enzymes called lipases. With a base the reaction becomes essentially irreversible, since carboxylate ions (formed from the acid) have little or no tendency to recombine with the hydroxyl groups of glycerol.

When hydrolysis takes place in the presence of alkali, the metal salt of the acid, called a *soap*, is obtained; the process by which it is formed is called *saponification*.



*Saponification* is used as a rapid test to determine the average chain length of acid groups attached to the glycerol molecule. An excess of potassium hydroxide solution of known concentration is added to a sample of the fat or oil; the mixture is boiled until the reaction is complete, after which the left-over unreacted base is titrated with acid. The shorter the acid chain, the more

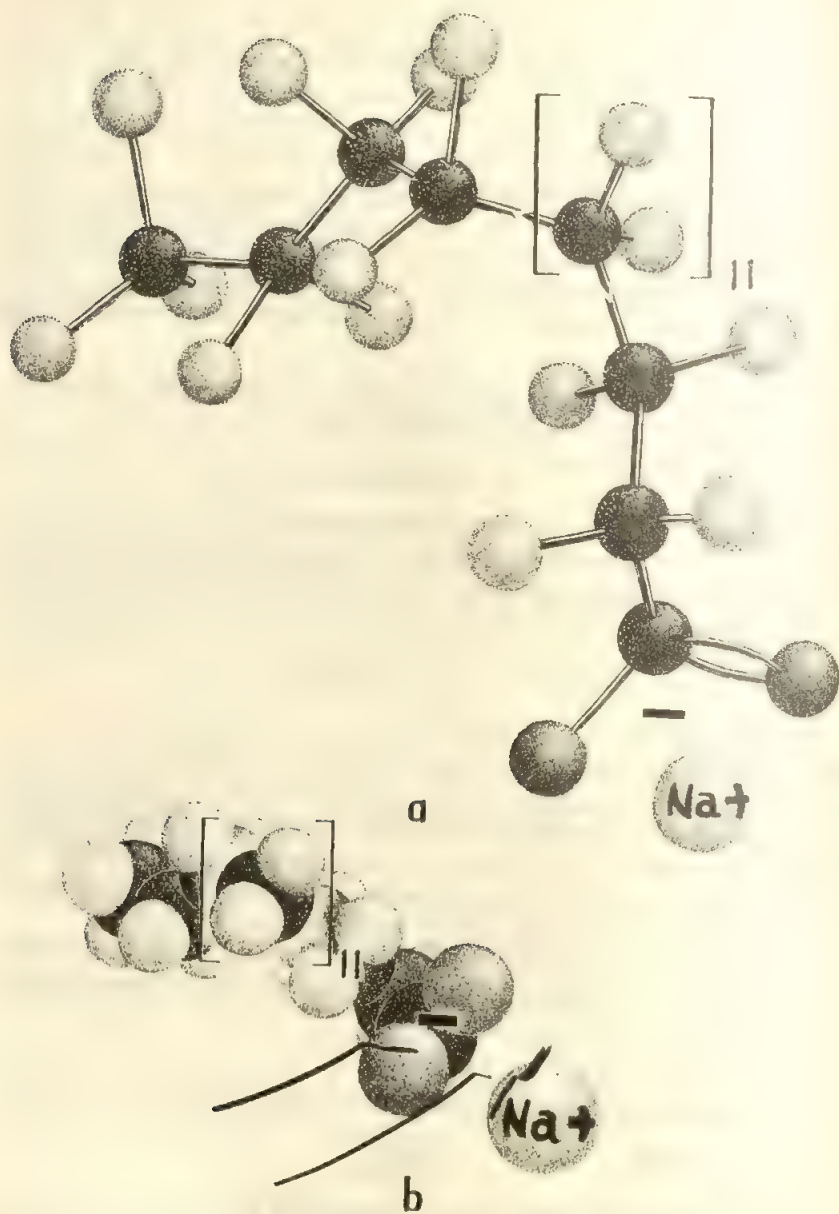


Figure 35.1. A typical soap molecule.

ester molecules are contained per gram of oil, and the greater the amount of potassium hydroxide required. The number of milligrams of potassium hydroxide required to saponify 1 g of oil is called the saponification number.

Soaps have been made for many years. The early American housewife saved beef tallow scraps and cooked them with lye-containing oak ashes until the reaction was complete, skimmed off the scum that formed, and poured the clear liquid in molds to harden.

The soap molecule is an interesting chemical. A characteristic soap molecule, sodium stearate, obtained from the saponification of stearin, is illustrated in Figure 35.1. It has a long hydrocarbon (petroleum-like) chain attached at one end to a negative carboxylate ion with its associated sodium ion. The molecule has a Dr. Jekyll and Mr. Hyde personality. The hydrocarbon end is

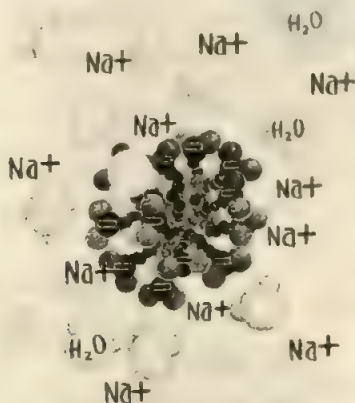


Figure 35.2. A soap micelle.

oil soluble; the carboxylate end loses its sodium ion in water, is negatively charged and soluble in water. Because of this, soap does not form a true solution in water. The insoluble oily ends of many molecules dissolve in each other, leaving the carboxylate ions, bereft of their associated sodium ions, sticking out around the outside (Fig. 35.2). The tiny, highly charged oil drop, called a micelle, is attached to polar water molecules and remains suspended in the water phase.

A soap solution is not a true solution but a colloid. The particles in solution are not molecules, but aggregates of many molecules. The colloidal solution is quite stable, because the charged micelles repel one another. They can be made to precipitate only by neutralization of the charge. Any calcium or magnesium with their doubly charged ions present in the solution are attracted to the micelles, neutralize them and allow them to collect. Sodium or potassium ions remain free in solution.

The cleansing action of soap is illustrated in Figure 35.3, which shows a soap micelle meeting an oil droplet. The oily ends of the soap molecules dissolve in the droplet, making a larger micelle still charged sufficiently to be carried off in the water. This double-acting ability of soap to make two

insoluble phases compatible makes it a detergent. All detergents act in a similar manner. The increased use of soap, with its ability to "cut" grease and oil and to remove bacteria embedded in the oils, has been partially responsible for the increase in life expectancy of the human race.

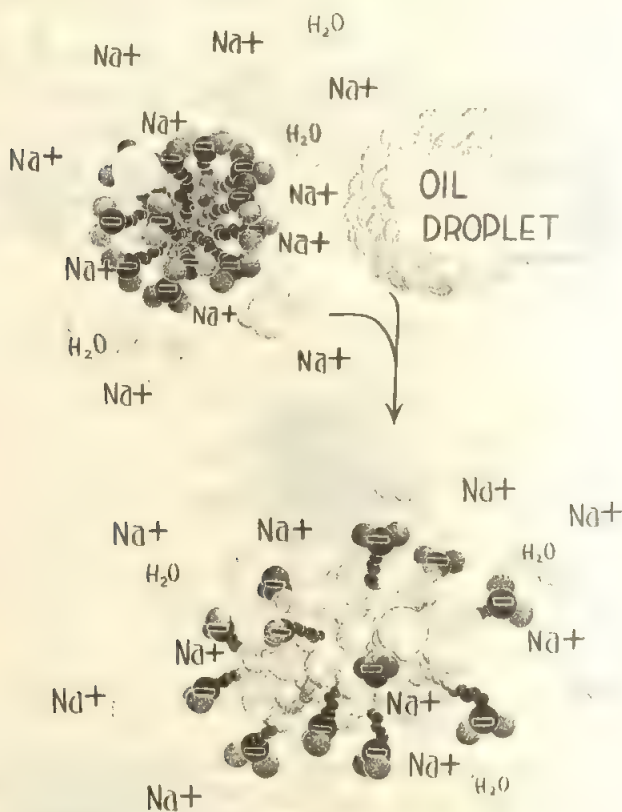
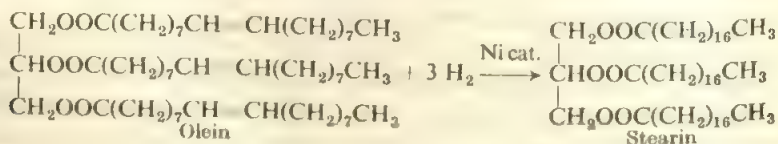


Figure 35.3. The action of soap.

### B. ADDITION REACTIONS

Since most fats and oils contain unsaturated fatty acids, a variety of addition reactions is to be expected. Typical of these reactions are those with hydrogen and the halogens.

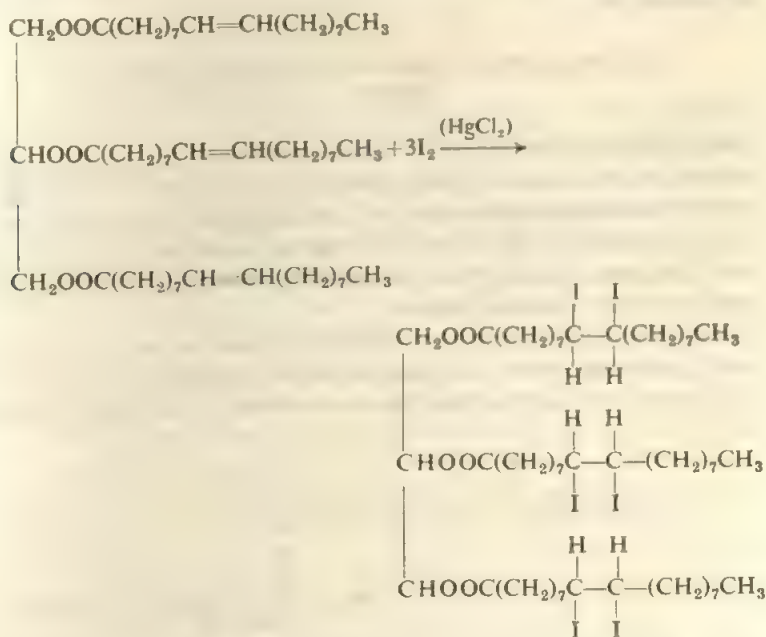
(1) *Hydrogenation of oils* in the presence of a nickel catalyst results in the addition of hydrogen to carbon-carbon double bonds of the unsaturated fatty acids present. For example, olein may be converted to stearin by this means:





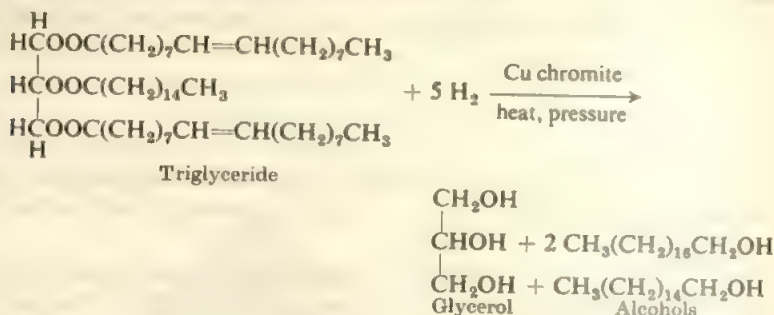
This reaction is of great industrial importance since it permits the transformation of inexpensive, unsaturated vegetable oils into fats which the American housewife finds desirable for household use. Industrially the hydrogenation is generally not continued to completion, but only until the melting point has been raised sufficiently to yield a fat of the proper consistency. Cottonseeds, soybeans and peanuts are excellent sources of oils which may be hydrogenated to give a good cooking fat. Most present day shortenings are "hydrogenated vegetable oil." Butter substitutes (margarines) produced by this method are further modified by adding vitamin supplements, coloring and flavoring to simulate butter. This hydrogenation of oils to fats is often referred to as "hardening" of fats.

(2) Among other reagents which *add readily to unsaturated bonds in fats and oils are the halogens*. The addition is quantitative. Samples of oils are treated with iodine solution to determine their degree of unsaturation and therefore the feasibility of hardening them to make shortening. To determine how much iodine adds, an excess of a specially prepared solution of a known iodine concentration is added to a sample of the oil; the mixture is allowed to stand for a time, and the iodine remaining is measured by titration. The grams of iodine which have been added to 100 grams of the oil are calculated. This is referred to as the oil's "iodine number." A representative equation showing the addition of iodine to olein (glyceryl trioleate) follows:

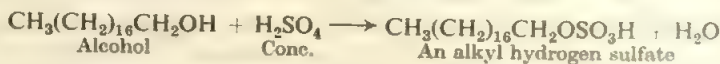


(3) When the *hydrogenation of a fat or oil* is carried out using *copper chromite under pressure* and at higher temperatures, in addition to adding hydrogen to the carbon-carbon double bonds present, the reduction of

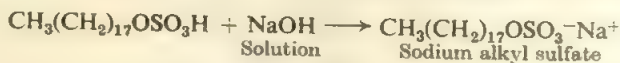
the carbonyl groups and the cleavage of the ester linkages are accomplished. The reaction is illustrated with  $\alpha, \alpha'$ -dioleo- $\beta$ -palmitin.



This reaction is carried out on a large scale commercially. The long chain fatty alcohols are treated with sulfuric acid to yield alkyl hydrogen sulfates. These

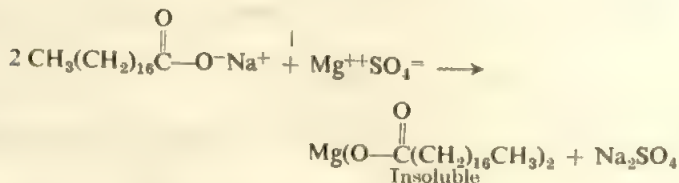


alkyl hydrogen sulfates are moderately strong acids; they are much stronger than carboxylic acids. Neutralization with sodium hydroxide solution yields the sodium salt.



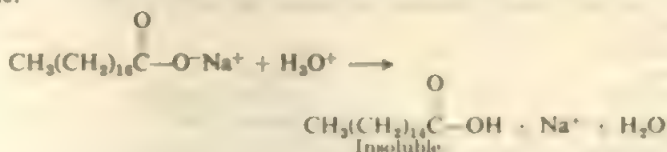
Like soap, this molecule has two natures, one due to a long, oil soluble chain and the other to a water soluble ionic end. Like soap, it is a detergent, one of the synthetic detergents used for laundering clothes and washing dishes. The detergents form micelles in water and surround and carry off oil droplets much the same as soap. These so-called "synthetic detergents" have advantages over soap as cleaning agents.

Magnesium and calcium ions present in "hard water" cause the soap to form a precipitate which is lighter than water. Not only is the soap unable to aid in cleansing, but the insoluble curd adheres to the fabric being washed.



The magnesium and calcium salts of the alkyl hydrogen sulfates are soluble. The detergent molecules are neither precipitated nor hindered in their cleansing.

Soaps are not effective cleansing agents in weakly acid solutions, such as a solution containing fruit juices, because soap ion gains a proton and becomes insoluble.



Detergents do not take protons from weakly acid solutions, but remain soluble and active.

### C. BIOLOGICAL SIGNIFICANCE

It is well known that fats are stored in many different places in the body and serve a number of important functions. The stored fat serves as (1) a protection to the body and its vital organs against bruises and shock damage, (2) an insulator to prevent excessive heat loss and (3) a support for the different organs in the body. Fats also are the most concentrated source of energy to the organism, yielding per gram over twice as many calories as do carbohydrates and proteins:

Fat	→ 9 cal/gram
Carbohydrate	→ 4 cal/gram
Protein	→ 4 cal/gram

Thus fat is the most efficient way of storing calories. This stored fat, referred to in man as depot fat, may be called on to furnish fuel and energy when the need arises. With the exception of certain unsaturated fatty acids, however, lipid is not essential in the diet, a fact which implies merely that most lipids can be synthesized by man from other dietary constituents at a rate adequate for normal requirements of growth and health.

When the diet consists of an excess of a carbohydrate such as starch (Chapter 39), fat is deposited. It may be inferred from this that starches, when in the diet in excess of actual needs, may be converted into fats by the animal body. This process is referred to as fat synthesis.

Studies concerned with the breakdown of starches in animals, including man, have shown that glucose, the simple carbohydrate from which starch is formed, is degraded inside cells into a very reactive two-carbon organic compound which the body uses to make fatty acids. By combining eight of these two-carbon units together, a fatty acid, stearic acid, is obtained. If seven units are used, palmitic acid results. Esterification of these fatty acids with glycerol (also formed from glucose through a different series of reactions) produces a fat or oil, which is then transported to fat depots and stored, as fats taken directly in the diet are stored. This process serves as a means for storing the excess energy derived from starches in the most efficient way available to the organism.

## EXERCISES

1. How does cottonseed oil differ structurally from petroleum oil?
2. What structural feature is identical in all animal and vegetable oils?
3. Define:
  - a. glyceride
  - b. ester
  - c. fatty acid
  - d. oil
  - e. fat
  - f. saponification number
  - g. iodine number
  - h. soap
  - i. detergent
  - j. "synthetic" detergent
  - k. "hardened" oil
  - l. micelle
  - m. lipid
4. Write a representative equation, showing special conditions and catalysts for:
  - a. the saponification of a fat
  - b. the hydrogenation of a fat with a nickel catalyst
  - c. the hydrogenation of a fat with with copper chromite catalyst
  - d. addition of iodine to a fat
5. Write structural formulas for each:
  - a. a fat
  - b. an oil
  - c. shortening
  - d. soap
  - e. synthetic detergent
  - f. glycerol
  - g.  $\beta$ -stero- $\alpha,\alpha'$ -dipalmitin
  - h. palmityl hydrogen sulfate
  - i. sodium stearyl sulfate
  - j. oleic acid
6. Write equations showing the preparation of a synthetic detergent, beginning with the natural fat palmitin. Show catalysts and other special conditions.
7. Write equations accounting for the failure of soap as a cleansing agent in (a) weakly acid solutions and (b) hard water.
8. Which type of food—protein, fat or carbohydrate—contributes the most energy per gram when oxidized completely in the body?
9. Explain the action of detergents.



## ORGANIC COMPOUNDS OF NITROGEN, PHOSPHORUS AND SULFUR

Organic compounds containing nitrogen, phosphorus and sulfur are relatively abundant and are widely distributed in nature in a great variety of substances. Many of these substances are key compounds in living organisms. They induce important physiological responses in plants and animals. Proteins (nitrogen-containing compounds; Chapter 38) mediate the rates of almost all biological reactions. Organic phosphorus compounds are present in all living cells and actively participate in the dynamic processes by which food is converted into usable energy. Many substances must be phosphorylated (combined with phosphoric acid) before undergoing changes in living systems. The amino acid cystine (Chapter 38), a nitrogen-sulfur-organic compound, is the main structural unit in hair, fingernails and animal hoofs. The polymer nylon contains nitrogen.

Many organic compounds of these elements are either synthesized or isolated for use in medicine and agriculture.

### 1. COMPOUNDS OF NITROGEN

Of the many types of organic nitrogen-containing compounds, amines and related compounds are the most important and will be discussed in detail. Amines are organic bases closely related to ammonia in structure and in chemical behavior. Amines may be considered as formed from ammonia by replacing *one or more* hydrogens with alkyl or aryl groups.

Depending upon the number of alkyl or aryl groups introduced, amines are classified as primary, secondary or tertiary (Fig. 36.1).

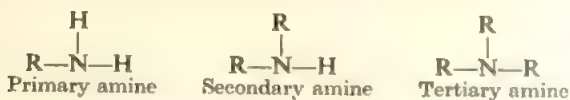
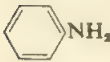
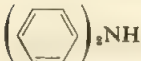
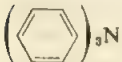
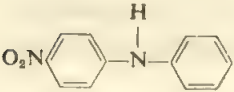
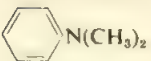


Figure 36.1. Classes of amines.

Specific examples of a primary, secondary and tertiary amine are given in Figure 36.2. Ammonia is included to emphasize the close structural relationship.

Table 36.1. Amines

<i>Formula</i>	<i>Classification</i>	<i>Name</i>
$\text{CH}_3\text{NH}_2$	Primary; aliphatic	Methyl amine
	Primary; aromatic	Aniline (Phenylamine)
$(\text{CH}_3\text{CH}_2)_2\text{NH}$	Secondary; simple aliphatic	Diethylamine
	Secondary; simple aromatic	Diphenylamine
$(\text{CH}_3\text{CH}_2\text{CH}_2)_3\text{N}$	Tertiary; simple aliphatic	Tri- <i>n</i> -propylamine
	Tertiary; simple aromatic	Triphenylamine
$\begin{array}{c} \text{H} \\   \\ \text{CH}_3\text{CH}_2\text{NCH}_3 \end{array}$	Secondary; mixed aliphatic	Ethylmethylaniline
	Secondary; mixed aromatic	p-Nitrophenylphenyl-amine
	Tertiary; mixed aromatic-aliphatic	Dimethylaniline (Dimethylphenylamine)

Primary amines may be either aliphatic or aromatic. In accordance with the practice followed in the classification of ethers, secondary and tertiary amines are referred to as simple or mixed, depending on the similarity of the organic groups attached to the nitrogen atom. Diphenylamine is a simple aromatic amine. Ethylmethylaniline is a mixed aliphatic amine. Other examples are given in Table 36.1.

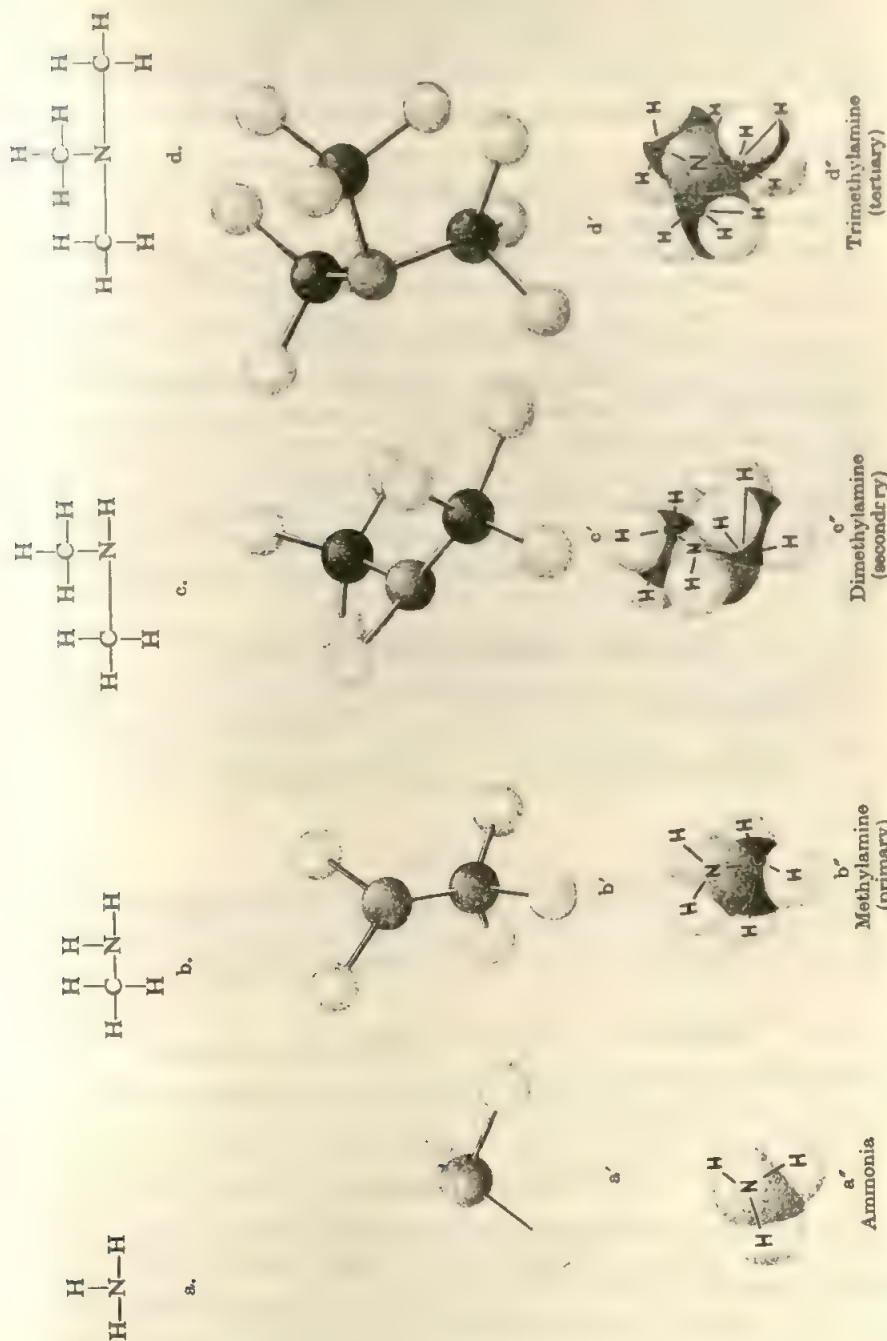


Figure 36.2. Structure of the methyl amines.

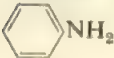

## A. NOMENCLATURE

Common names for amines are obtained by naming the groups attached to the nitrogen atom, followed by the term "amine." For example,  $\text{CH}_3\text{CH}_2\text{NH}_2$  is ethyl amine,  $(\text{CH}_3)\text{NH}(\text{CH}_2\text{CH}_3)$  is ethylmethylaniline and  $(\text{C}_6\text{H}_5)_3\text{N}$  is triphenylamine. Table 36.1 provides examples of other names. The similarity of this system to that used for naming ethers and ketones should be apparent. Names of amines formed in this manner are also approved systematic IUPAC names.

Aromatic amines related to aniline (phenylamine), particularly the mixed amines, are usually named as aniline derivatives. Thus the compound which has a methyl group substituted for one of the hydrogen atoms attached to the nitrogen of aniline is named monomethylaniline. If two methyl groups are present in place of hydrogens, the compound is named dimethylaniline. Common names of ring substituted aromatic amines are formed in a similar way. Some aromatic amines have special names. Meta-toluidine, for example, is a name often used for meta methyl aniline.

Systematic IUPAC names may be formed also by considering amines as amino ( $-\text{NH}_2$ ) or substituted amino ( $-\text{NHR}$  or  $-\text{NR}_2$ ) hydrocarbons. Systematic names for several amines derived in this way are listed in Table 36.2.

Table 36.2. Amines—Systematic Names

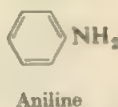
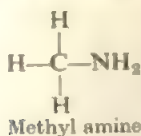
$\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$	1-Aminopropane
$\begin{array}{c} \text{CH}_3\text{CHCH}_2\text{CH}_2\text{CH}_3 \\   \\ \text{NH}_2 \end{array}$	2-Aminopentane
$\text{CH}_3\text{CH}_2\text{NHCH}_2\text{CH}_2\text{CH}_3$	1-(N-Ethylamino)propane
	Aminobenzene (aniline)
	N-Ethylamino benzene

## B. PHYSICAL PROPERTIES

Methyl amine, dimethyl amine and trimethylamine are very soluble gases which have a strong ammoniacal, or fishy, odor. They are flammable. Higher amines of the aliphatic series are liquids or colorless solids and exhibit decreasing solubility with increasing molecular weight. On the other hand, the aromatic amines all are liquids or solids. They are colorless when freshly prepared, but become dark brown or red on standing. They have a peculiar



nonammoniacal odor and are, in general, much less soluble in water than aliphatic amines. *Methyl amine* is the simplest of the alkyl amines, and *aniline* is the simplest of the aromatic amines. As with the alcohols and aldehydes, to be aromatic, the key atom or group (in this case nitrogen) must be joined directly to a benzene or benzene-like ring. The structures of these amines are given below, followed by a brief description.



### PROPERTIES OF SPECIFIC COMPOUNDS

(1) **Methyl amine.** Methyl amine occurs in fish (herring) brine, in the urine of dogs and other animals fed on a high protein diet, and in certain plants. In most respects it has properties very similar to ammonia. For example, it is very soluble in water. One volume of water dissolves 959 volumes of the amine at 25°C. It is soluble in alcohol and completely miscible with ether. The primary use for methyl amine is in the tanning of leather and in organic synthesis. It is manufactured by the ton for these uses.

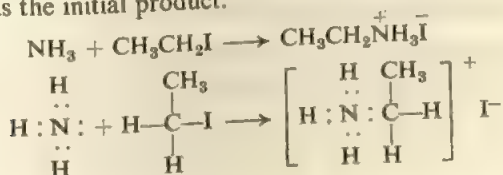
(2) **Aniline.** Aniline (phenyl amine) was first obtained in 1826 by the dry distillation of indigo. It is an oily, colorless liquid which rapidly darkens on exposure to air and light. It is flammable and volatile with steam (b.p. 184–186°C; m.p. –0.6°C). The compound is much less soluble in water than is ammonia or methyl amine (1 g dissolves in 28.6 ml of water), but it is miscible with alcohol, benzene and most organic solvents. Aniline is toxic; serious poisoning may result from the ingestion of as little as 0.25 cc.

### C. PREPARATION

Two reactions used for the preparation of amines will be considered, *alkylation* (of ammonia with alkyl halides) and *reduction* (of nitro compounds or nitriles). Special reactions for preparing specific amines will not be described.

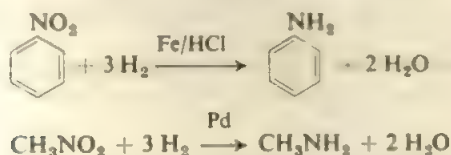
#### (1) ALKYLATION

Alkylation is the most direct method for preparing amines and refers to the reaction between ammonia or amines and an alkyl halide which introduces alkyl groups directly into the molecule in place of one or more hydrogens. The reaction between ammonia and ethyl iodide yields ethyl ammonium iodide as the initial product.





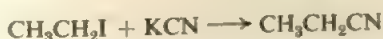
Nitro groups of both aromatic (nitrobenzene) and aliphatic (nitromethane) compounds may be reduced to give primary amines.



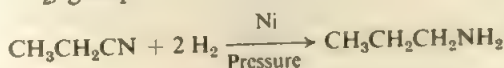
Since aromatic nitro compounds are readily prepared by direct nitration (Chapter 31), this procedure is the most common means of introducing an amino group into an aromatic ring. Aliphatic nitro compounds (Chapter 29) are less readily obtainable and are correspondingly less useful.

### (3) REDUCTION OF NITRILES (CYANIDES)

Organic compounds which have an alkyl or aryl group attached to a cyano ( $-\text{CN}$ ) group are known as nitriles or cyanides (Chapter 34). Their general formula is  $\text{RCN}$ , where  $\text{R}$  represents either an alkyl or an aryl group. Nitriles are readily prepared by replacing the halogen of an alkyl halide with the cyano group.



Nitriles, once obtained, are readily reduced by catalytic hydrogenation to give primary amines, the cyano group being converted into a methyleneamino ( $-\text{CH}_2\text{NH}_2$ ) group.



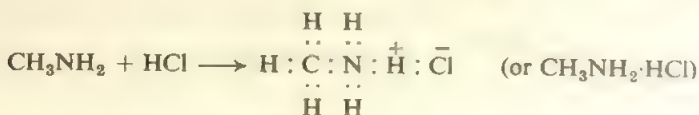
Examination of these two reactions shows that in the formation of the nitrile from the alkyl iodide, one carbon is added to the  $\text{R}$  group which, when the amine is formed, is converted into a methylene ( $-\text{CH}_2-$ ) group. The resulting primary amine therefore has one more carbon atom than the alkyl halide from which it was made. The reaction is used to increase the length of a carbon chain.

## D. REACTIONS

### (1) BASICITY

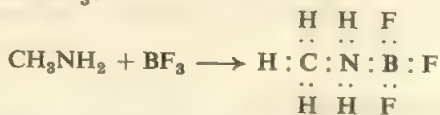
Basicity is the characteristic property of amines. It determines the types of reactions which they undergo and influences their physical properties. Like ammonia, the basicity of amines is due to an unshared (free) pair of electrons on the nitrogen atom. The chemical behavior of amines is, therefore, quite analogous to that of ammonia (Chapter 21). Amines, because of a free pair of electrons, are electron-rich molecules in the same sense as ammonia or the hydroxide ion. Correspondingly, amines seek the relatively most

positive site of other molecules with which to react chemically. For example, methyl amine reacts with hydrochloric acid, forming a hydrochloride salt.

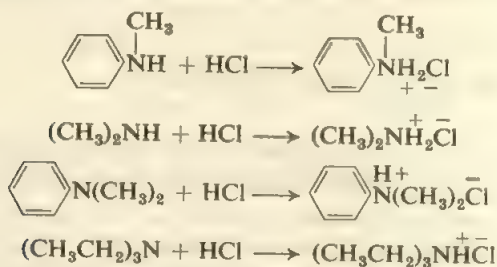


The driving force for this addition resides in the tendency of nitrogen to share its free electron pair with the positively charged proton of the hydrogen chloride. If the proton is combined with chloride when collision occurs, the chloride ion is displaced. If it is present in solution as the hydrogen ion, the positive ion merely becomes attached to the amine. The salt is named methyl ammonium chloride or methyl amine hydrochloride; the name methyl ammonium chloride is indicative of its similarity to ammonium chloride.

In a related reaction with boron trifluoride ( $\text{BF}_3$ ), which is an electron-deficient substance, methylamine, by providing both electrons for the bond, yields an amine-boron trifluoride analog of the salt formed when ammonia reacts with  $\text{BF}_3$ :



Secondary and tertiary amines undergo similar reactions with acids to form stable salts:






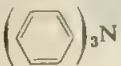
The readiness with which an amine accepts protons or reacts with other electron-deficient reagents depends on the availability of the unshared electrons, since these electrons are necessary for bond formation. An increase in the electron density about the nitrogen atom makes the unshared pair more available; a decrease makes these same electrons less available. Alkyl amines, in general, are stronger bases than ammonia. This fact is attributed to the nature of alkyl groups which are more electron-releasing than hydrogen. Alkyl groups induce an increased electron density on the nitrogen of amines above that of ammonia. The free pair on the nitrogen becomes more available, giving aliphatic amines their greater basicity.

On the other hand, aromatic amines are less basic than ammonia. Aryl



groups generally are electron-withdrawing and decrease the electron density about the nitrogen atom. The basicity of several amines is listed in terms of ionization constants in Table 36.3.

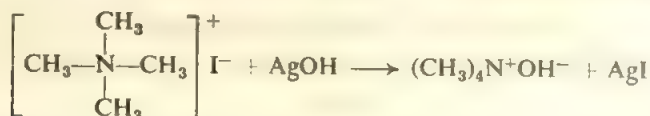
Table 36.3. Basicity of Amines

<i>Name</i>	<i>Formula</i>	<i>K<sub>b</sub></i>
Ammonia	NH <sub>3</sub>	$2 \times 10^{-5}$
Methylamine	CH <sub>3</sub> NH <sub>2</sub>	$4 \times 10^{-4}$
Aniline	 NH <sub>2</sub>	$5.4 \times 10^{-10}$
Dimethylamine	(CH <sub>3</sub> ) <sub>2</sub> NH	$5.4 \times 10^{-4}$
Methylaniline	 NH(CH <sub>3</sub> )	$2.5 \times 10^{-10}$
Trimethylamine	(CH <sub>3</sub> ) <sub>3</sub> N	$5.9 \times 10^{-5}$
Dimethylaniline	 N(CH <sub>3</sub> ) <sub>2</sub>	$2.4 \times 10^{-10}$
Triphenylamine	 N	less than $10^{-10}$

**Quaternary ammonium compounds.** Closely related to and derived directly from the amines are the quaternary ammonium salts and bases. Quaternary salts are formed when tertiary amines react with alkyl halides. Tetramethylammonium iodide, a typical quaternary ammonium salt, has the formula shown in Figure 36.3.

Structurally, this compound is related to ammonium iodide. It is a substituted ammonium iodide in which four hydrogens have been replaced with methyl groups. The properties of tetramethylammonium iodide verify this relationship. It is a solid with a high melting point (above 200°C). The compound is a true ionic salt and dissolves in water to give a solution which conducts an electric current. Other quaternary ammonium salts are similar. If one of the R groups is a long chain hydrocarbon, the salt takes on the properties of a detergent. Detergents of this class are known as *invert soaps* because the water soluble polar end is a positive rather than a negative ion. It might be recalled that the water soluble part of soap and the usual detergents is a negative carboxylate or sulfonate group.

Just as ammonium iodide can be converted into ammonium hydroxide by treatment with silver hydroxide (silver iodide precipitates), so tetramethylammonium iodide can be converted into tetramethylammonium hydroxide.



Tetramethylammonium hydroxide is a strong base. It readily absorbs carbon dioxide from air, just as sodium or potassium hydroxide does. An aqueous solution of this base is colorless, odorless, bitter, caustic and strongly alkaline

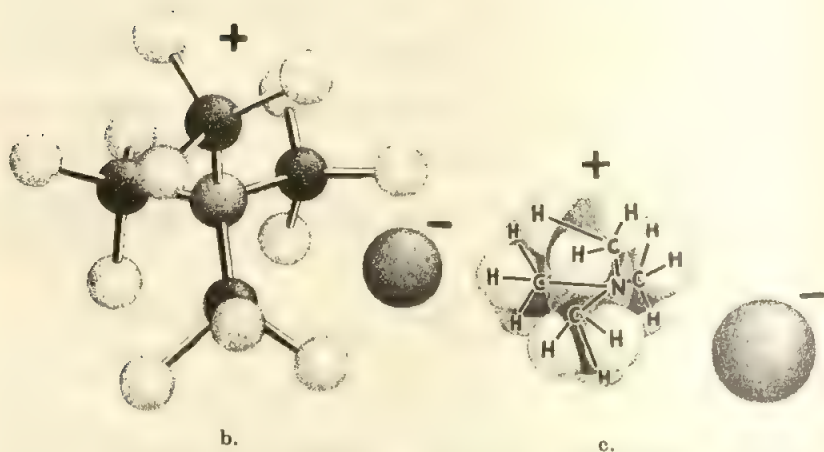
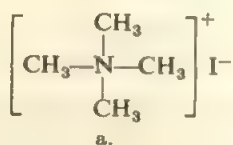
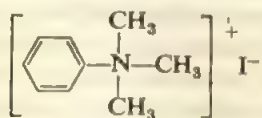


Figure 36.3. Tetramethylammonium iodide.

in the same sense as are solutions of alkali metal hydroxides. Like sodium hydroxide, tetramethylammonium hydroxide imparts a soapy feel to the skin. A quaternary salt having an aryl group is trimethylphenylammonium iodide.



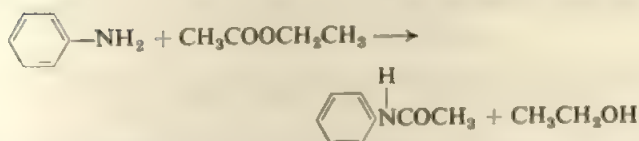
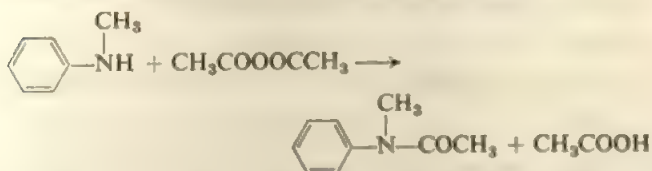
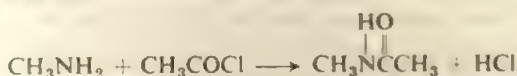
## (2) ALKYLATION

Alkylation of amines is a displacement reaction discussed previously (pp. 589–590).

## (3) ACYLATION

The reaction between a primary or secondary amine and an acid derivative (acid halide, acid anhydride or ester; see Chapter 34) yields an amine

derivative in which an acyl ( $\text{R}-\overset{\text{O}}{\underset{\text{||}}{\text{C}}}-$ ) group has been substituted for a hydrogen attached to the amine nitrogen. The term *acylation* is used because an *acyl group* is introduced into the molecule.



Tertiary amines which have no hydrogen attached to nitrogen do not undergo this reaction.

Acylation may be considered to be an acid-base reaction. The amine (a base) attacks the carbonyl carbon (positive center) of the acid derivative to displace a negative ion (i.e., chloride from an acid chloride). As a result of this loss of a negative ion, a positively charged complex remains which immediately adjusts (stabilizes) itself through loss of a proton to give the stable acylated amine. The reaction again reflects the electron-rich (basic) nature of amines and emphasizes the electron-deficient character of the carbonyl carbon atom. Having the most positive carbonyl carbon, acid halides react most readily, whereas esters, which have the least positive carbonyl carbon, react much more slowly.

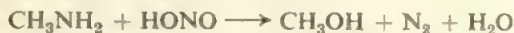
Close scrutiny of the formula of the product shows that two organic groups

are united by an  $\overset{\text{H}}{\underset{|}{\text{N}}}-\overset{\text{O}}{\underset{\text{||}}{\text{C}}}-$  group of atoms. This is called an *amide linkage*. It is present in acid amides (Chapter 34) and gets its name from these compounds. It is an important type of bonding commonly encountered in biologically interesting substances, particularly the proteins (Chapter 38).

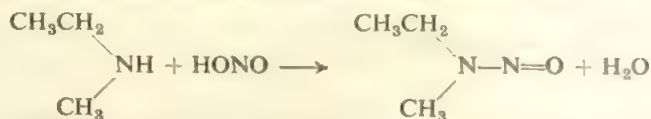
## (4) REACTION WITH NITROUS ACID

The products formed when amines react with nitrous acid depend on the amine used. Each class of amine exhibits different behavior.

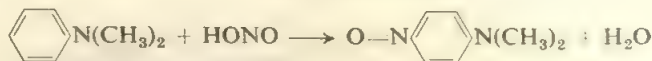
*Primary aliphatic amines* liberate gaseous nitrogen, the evolution of which serves as a useful test for amines of this class. The reaction is used also for the quantitative determination of free amino groups in proteins and amino acids by measuring the volume of nitrogen gas evolved. Aliphatic diazonium compounds which decompose immediately are formed as intermediates in this reaction.



*Secondary aliphatic and aromatic amines* form nitrosoamines. Nitrosoamines are usually yellow, neutral compounds which are insoluble in dilute mineral acids. When formed in aqueous solutions they separate as an oily layer, a behavior used as a test for secondary amines:

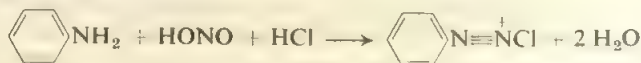


*Tertiary aliphatic amines* yield nitrous acid salts which dissolve in the aqueous medium. Substitution of the ring occurs with aromatic tertiary amines:



The reaction of nitrous acid with primary, secondary and tertiary aliphatic amines serves as a test for distinguishing between these three types of compounds because the different products formed can readily be detected.

The reaction of primary aromatic amines with nitrous acid is one of the most important reactions in organic chemistry. Primary aromatic amines react to form diazonium compounds (salts) which are stable at low temperatures in aqueous solution. The nitrous acid for this reaction is formed *in situ* by adding hydrochloric acid to a cold solution of sodium nitrite. Aniline and nitrous acid form benzene diazonium chloride:



The product formed is extremely useful because of the unique behavior of the diazonium ( $-\text{N} \equiv \text{N}^+$ ) group. Diazonium salts are versatile. The diazonium group may readily be replaced with a variety of other atoms or groups, or it may undergo a coupling reaction to form diazo compounds.

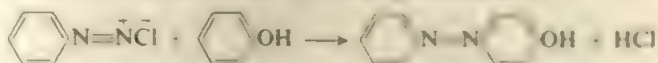
Replacement of the diazonium group is an excellent general method for introducing F, Cl, I, CN, OH and H into aromatic (benzene-like) rings. The equation for the introduction of iodine is:



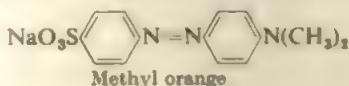
Coupling takes place with phenols and aromatic amines. Azo compounds, recognized by the *azo* ( $-\text{N}=\text{N}-$ ) group, are formed. Benzene diazonium



chloride reacts with phenol to give p-hydroxyazobenzene:



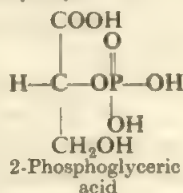
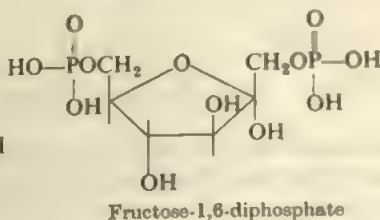
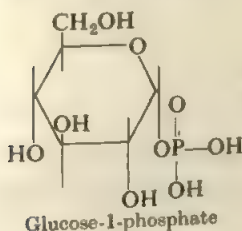
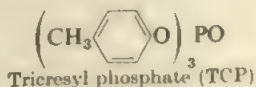
Most azo compounds are colored. Many are useful dyes or biological stains. About one-half the dyes in industrial use today are azo dyes. Methyl orange is an azo compound which you may have used as an acid-base indicator:



## 2. PHOSPHORUS COMPOUNDS

Many organic phosphorus compounds are important. Two types are of particular interest, alkyl phosphines and the organic esters of phosphoric acid. Alkyl phosphines are derived from phosphine ( $\text{PH}_3$ ) and may be said to resemble amines in structure. They are less basic and more subject to oxidation than are amines. Phosphine itself burns spontaneously in air. The basicity of phosphines increases with the introduction of alkyl groups. Table 36.4 lists the known types of phosphine compounds.

Esters are perhaps the most important, and certainly the most frequently encountered, organic phosphorus compounds. Esters of phosphorus, phosphoric and pyrophosphoric acids are known. *Tributyl phosphate* and *tricresyl phosphate* (TCP), widely used plasticizers, are triesters of phosphoric acid. Monophosphate esters of phosphoric acid with glucose, fructose and other carbohydrates (Chapters 39 and 40) are significant biological compounds. Glucose-1-phosphate, fructose-1,6-diphosphate and 2-phosphoglyceric acid are three of the recognized metabolites formed during both the fermentation of glucose and also in its transformation in muscle. The structures of several of these compounds are as follows:

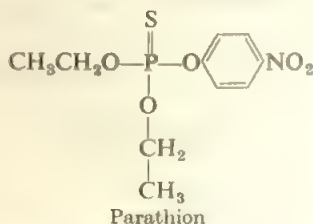
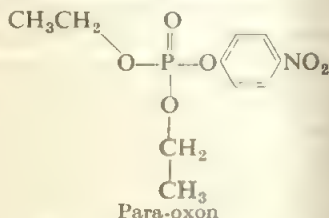
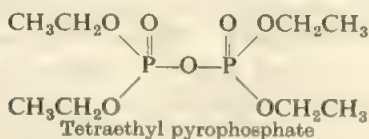


In contrast to the metabolites mentioned in the previous paragraph, certain organic phosphorus compounds are extremely toxic and are used as insecticides. Tetraethyl pyrophosphate, one example, useful for control of aphids, mites and red spiders, is an ester of pyrophosphoric acid. Para-oxon (diethyl

Table 36.4. Alkyl Phosphines

<i>Formula</i>	<i>Classification</i>
$\text{RPH}_2$	Primary
$\text{R}_2\text{PH}$	Secondary
$\text{R}_3\text{P}$	Tertiary
$\text{R}_4\text{P}^+$	Quaternary

*p*-nitrophenol phosphate) is a phosphoric acid ester with good insecticidal properties. Parathion, the corresponding thiophosphate (Diethyl *p*-nitrophenol thiophosphate), is also an effective insecticide and is more widely used than para-oxon. The formulas for these compounds are as follows:



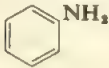
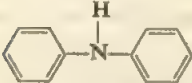
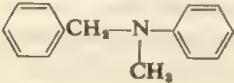
### 3. SULFUR COMPOUNDS

Sulfur compounds are important, particularly in the field of dyes and medicinals. They are closely parallel in structure to the compounds of oxygen discussed in earlier chapters of this text. The similarity is shown in Table 36.5, which lists the important oxygen compounds and their corresponding analogs.

Many other types of compounds might be compared, but the compounds listed in Table 36.5 are sufficient for illustrating the point that sulfur occupies the same position in sulfur compounds that oxygen does in similar oxygen-containing substances. Although in accord with their structural similarity many reactions of sulfur compounds are similar to those of oxygen compounds,



## EXERCISES

- Why is nitrogen an important element in organic compounds?
- Define the following and give an example for each term starred (\*):
  - \*an amine
  - \*a primary amine
  - \*a secondary amine
  - \*a mixed secondary amine
  - \*an alkyl aryl amine
  - \*alkylation of an amine
  - reduction
  - basicity
  - \*a tertiary amine
  - \*a quaternary ammonium salt
  - \*an invert soap
  - acylation
  - \*nitrosoamine
  - amide linkage
- Write two names for each:
  - $\text{CH}_3\text{—CH}_2\text{—NH}_2$
  - $(\text{CH}_3\text{CH}_2)_2\text{NH}$
  - 
  - $(\text{CH}_3)_4\text{N}^+\text{I}^-$  (one name)
  - $\text{CH}_3\text{—}\overset{\text{O}}{\parallel}\text{C}\text{—NH—CH}_3$  (one name)
  - 
  - 
- Write equations for the preparation of aniline, starting with benzene and a concentrated mixture of sulfuric and nitric acids.
- Write structural formulas for all the organic products formed when methyl iodide reacts with ammonia.
- List in the order of increasing basicity: (a) ammonia, (b) sodium hydroxide, (c) water, (d) ethyl alcohol, (e) aniline, (f) hydrochloric acid, (g) propylamine.
- Write an equation for the reaction between aniline and benzoyl chloride.
- What reagent might one use to distinguish methyl amine, dimethyl amine and trimethyl amine? Write reactions.



# STEREISOMERISM: GEOMETRICAL AND OPTICAL

No course in organic chemistry, regardless how brief, is complete without an introduction to stereoisomerism, an isomerism in which differences between isomers may be so slight that many of their physical and chemical properties are identical, but an isomerism important for living organisms because only one of two isomers may be found in nature; for example, one isomer may be an insecticide, the other not. An understanding of stereoisomerism is necessary for a study of carbohydrates and for a full appreciation of amino acids, proteins, and other naturally occurring compounds.

## 1. GEOMETRICAL ISOMERISM

The more obvious and lesser important kind of stereoisomerism is known by the non-definitive name *geometrical isomerism*. It occurs because of restricted rotation about a double bond. Because the double carbon to carbon bond is rigid, there are two 2-butenes: cis-2-butene and trans-2-butene (Fig. 37.1).

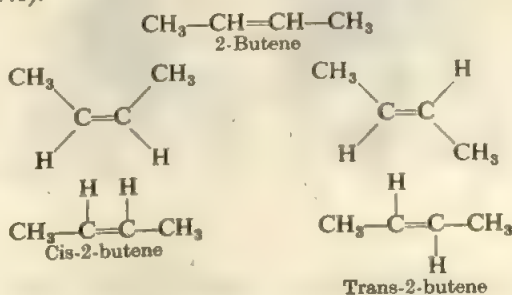


Figure 37.1. Cis- and trans-2-butenes.

In *cis*-2-butene, like groups attached to the carbons of the double bond appear on the same side of an imaginary line passing through the centers of the two carbons. In *trans*-2-butene, like groups appear on opposite sides of the extended line through the two carbons of the double bond.

Geometrical isomerism could have been introduced in the discussion of the cycloalkanes; *trans*-1,3-dimethyl cyclohexane obviously differs in structure from *cis*-1,3-dimethyl cyclohexane (Fig. 37.2).

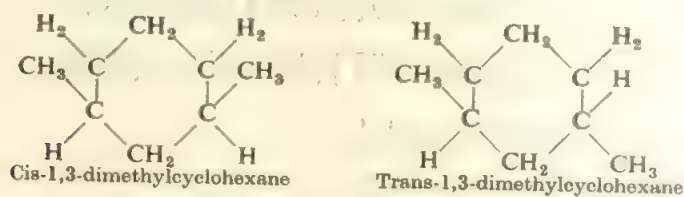


Figure 37.2. An example of *cis-trans* isomerism.

However, similarities between the pairs of isomers (Table 37.1) were so great, that it was almost unnecessary to distinguish one from another. *Cis*- and *trans*-isomers *can* be very different both physically and chemically. Consider *cis*- and *trans*-butendioic acids, known as maleic acid and fumaric acid respectively (Fig. 37.3). Physical properties of the two acids are

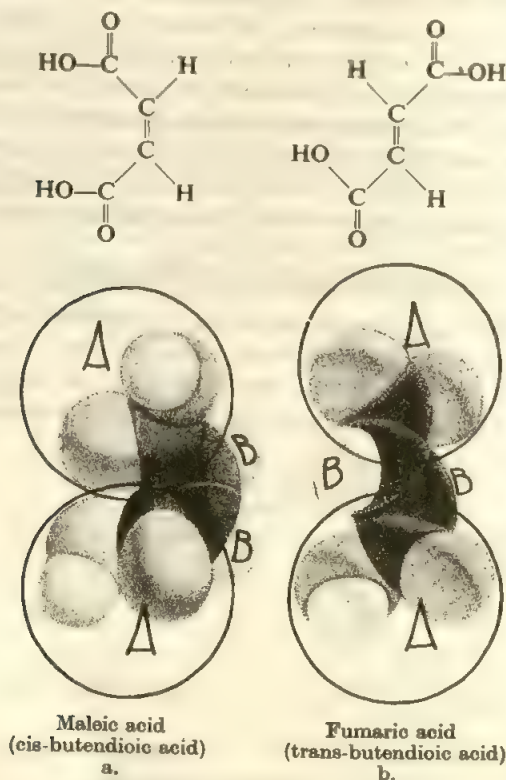
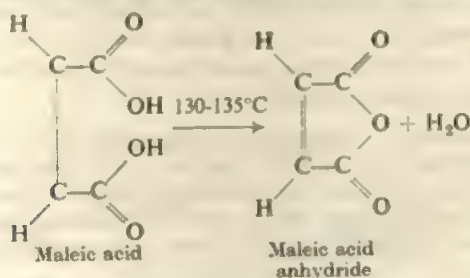


Figure 37.3. The butendioic acids.

Table 37.1. Physical Properties of Some Cis-Trans Isomers

	Melting Point	Boiling Point	Density	Solubility in Water g/100 ml of Water
Cis-2-butene	—	1.0	0.635	Insoluble
Trans-2-butene	—	2.5	0.635	Insoluble
Cis-1,3-dimethylcyclohexane	85	121.0	1.4269	Insoluble
Trans-1,3-dimethylcyclohexane	—	119.0	1.4254	Insoluble
Maleic acid (cis-butendioic acid)	130	Decomposed at 135	1.590	78.8
Fumaric acid (trans-butendioic acid)	287	290	1.630	0.70

compared in Table 37.1. One can see that maleic acid is a polar molecule, whereas fumaric acid is not. Because of the difference in structure, one chemical reaction of maleic acid is not readily available to fumaric acid. Maleic acid forms an acid anhydride when heated to 140°C.



Heating fumaric acid does not yield a monomolecular anhydride, for the carbonyl groups are held apart. Chemical differences are exemplified by the fact that fumaric acid is an intermediate in metabolic processes, whereas maleic acid is toxic.

## 2. OPTICAL ISOMERISM

The other type of stereoisomerism, *optical isomerism*, is much more important in this study than geometrical isomerism. Nevertheless, the differences between isomers are more subtle. Many years of investigation were required before the principles of optical isomerism were understood. Space does not allow a historical development of the concepts involved. Instead a specific example of isomerism (one important historically) will be considered.

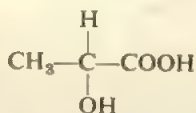
### A. THE LACTIC ACIDS

In 1780 an acidic substance was isolated from sour milk by Scheele. The substance, called lactic acid, was a product of the fermentation of milk sugar.

In 1807 Berzelius discovered a *similar* substance, an extract from muscle tissue. During the next half century the acid found in sour milk and the muscle extract were found to be remarkably alike. *Both substances:*

- (1) have the same molecular formula,  $C_3H_6O_3$ .
- (2) have the same melting point ( $26^\circ\text{C}$ ) and the same boiling point ( $122^\circ\text{C}$  [15mm]).
- (3) are hygroscopic (i.e., they absorb water from the atmosphere).
- (4) are very soluble in both water and organic solvents.
- (5) are decomposed by hot sulfuric acid to acetaldehyde and formic acid.
- (6) are oxidized to acetic acid and carbon dioxide.
- (7) have the same functional groups—a hydroxy group and a carboxyl group.

In fact, the functional groups occupy the same position. Each substance has the same structural formula:



and the same name,  $\alpha$ -hydroxypropionic acid (2-hydroxypropanoic acid). The evidence is overwhelming. With much less data, the compounds would have been “proven” to be identical, were it not for the fact that the plane of plane polarized light is rotated clockwise when passed through a solution of the muscle extract, but is unaffected when passed through a solution of the compound (as then prepared) from sour milk.

**Polarization and the Polarimeter.** Plane polarized light is light that has passed through a polarizer. A polarizer is a crystal or a film that allows only that component of light vibrating in one direction to pass through. When ordinary light vibrating in all directions perpendicular to the direction it is traveling falls upon the polarizer, only half passes through. Figure 37.4 shows light vibrating in three

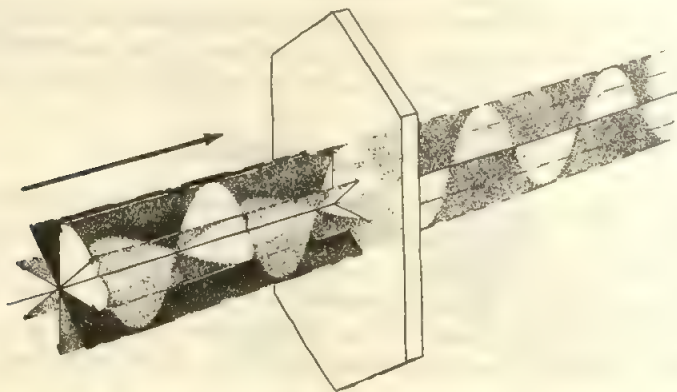


Figure 37.4. Plane polarization of light.

directions approaching the polarizer. That parallel to the crystal passes through unchanged; that perpendicular is stopped completely; and only the parallel projection of that vibrating on a  $45^\circ$  angle (to the crystal) passes through.



This is true, also, for a second polarizer (Fig. 37.5B) placed behind and exactly perpendicular to the first (Fig. 37.5A) lets no light pass through. Only when they are exactly "crossed" is the light excluded completely.

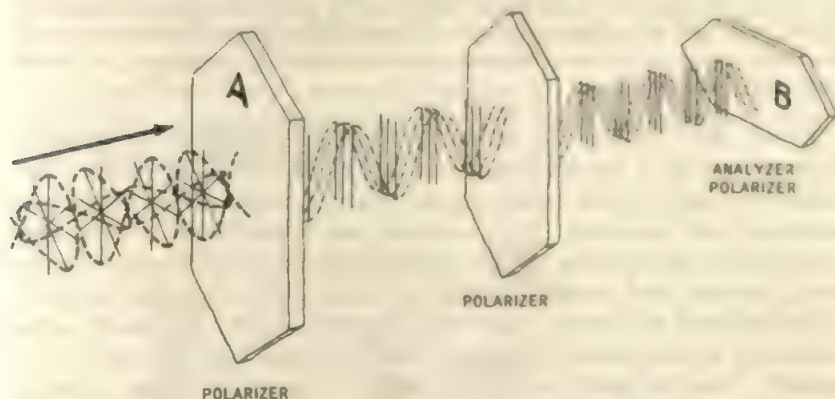


Figure 37.5 Total exclusion of light by "crossed" polarizers.

The polarimeter used to measure the optical rotation of solutions (Fig. 37.6) is arranged so that light passes through a polarizer, through the solution to be tested and through a second polarizer (analyzer) that can be rotated. The scale

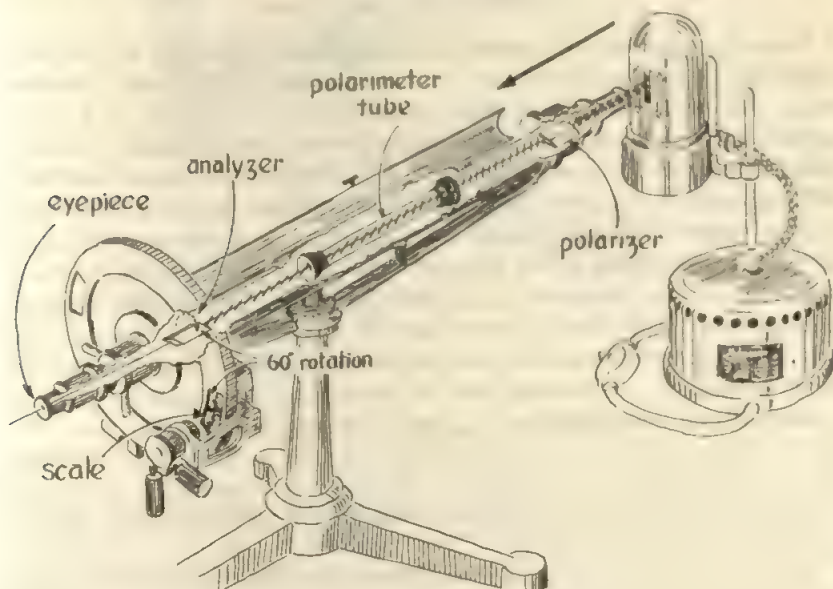


Figure 37.6. A polarimeter.

measuring rotation reads zero when the two polarizers are perpendicular to one another. If the light is excluded when the second polarizer is at zero (perpendicular to the first), the solution has no optical rotation, and is optically inactive. If the second polarizer must be rotated clockwise to exclude all the light, the solution is

optically active; it is said to rotate light to the right, or in the positive (+) direction. If the second polarizer must be turned counterclockwise, the solution rotates light to the left, or in the minus (−) direction.

The number of degrees (the magnitude) of rotation depends on the nature of the substance dissolved, the distance (length of the path) the light travels through the solution, and the concentration of the solution. For the purpose of this course, it shall be sufficient to know that some solutions rotate light positively (+); some rotate light negatively (−).

In the study of the two seemingly identical compounds, investigators eventually came to the conclusion that the muscle extract was a pure substance, and that the acid removed from sour milk was a mixture of the pure substance and an isomer. This conclusion was reached when another acid, tartaric acid, also optically inactive, was separated by Louis Pasteur into two equal portions, each of which rotated light equally but in opposite directions. From this work of Pasteur it came to be expected that if one optically active substance existed another did also with an equal and opposite optical activity. This has been proven to be the case. The acid in muscle tissue is a pure isomer, and therefore rotates the vibrational plane of light, whereas that obtained from sour milk contains an equal amount of both isomers. Each isomer rotates light but in an opposite direction, making it appear that no rotation has taken place.

## B. ASYMMETRIC MOLECULES

Pasteur's separation of seemingly optically inactive tartaric acid is most ingenious. His observations gave the key to possible differences in the isomers. He found that the sodium ammonium salt of tartaric acid, when crystallized from a solution, formed distinctive hemihedral crystals. Furthermore, two kinds of crystals formed. The crystals were almost identical, differing only in the sense that the *left hand* differs from the *right hand*. Pasteur separated the two types of crystals with a pair of tweezers. Solutions of these were optically active, of equal magnitude, but of opposite direction.

In 1874 Jacobus Hendricus van't Hoff and Joseph Achille LeBel independently presented the theory of optical activity accepted today. They saw that just as some crystals could be to one another as right and left hands, so could some molecules. A molecule that is asymmetric (that has no *plane of symmetry*) will be optically active, and will be one of a pair of isomers. The other isomer will be its *mirror image* and will differ as the right hand differs from the left hand, and its solutions will rotate light equally in the opposite direction. Any molecule in which a carbon atom is attached to four *different* groups is asymmetric (Fig. 37.7).

Because the bonds from the carbon atom do not lie in a plane, as it appears in the formula, but are directed to the corners of a regular tetrahedron, there exist two possible arrangements of the four groups.

Note first the hands in the figure. The left hand holding the model appears as a right hand in the mirror. Compare the right hand with the left hand, the arrangement of thumb and fingers and the palm and back of the hand.

Though the right hand has the same groups, it is the mirror image of the left hand. The right and left hand are different; they are not superimposable. One cannot place his or her hands together in any way to have them exactly the same. Because a hand has four different aspects, the back, the palm, the fingers and the thumb, it is not symmetrical; it is asymmetric and there exists another arrangement, its mirror image, which is not the same. Were it symmetrical, were there a plane of symmetry in the molecule so that one half of it were a mirror image of the other half, a non-identical mirror image of the whole would be impossible.

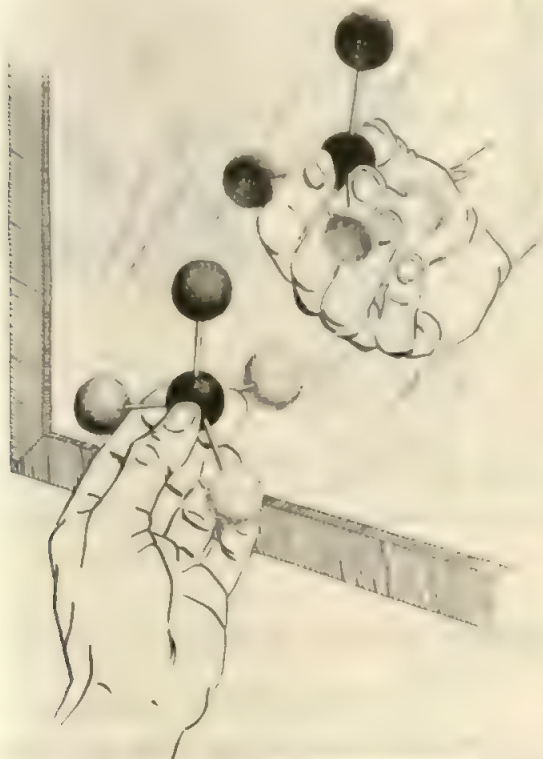


Figure 37.7. An asymmetric molecule.

Now study the model being held in Figure 37.7. Observe that four different groups are attached to the central atom held between the fingers. Just as the left hand holding the model appears in the mirror as a right hand, the molecule appears as its mirror image. Again, because the four groups are different, the mirror image has a different arrangement from that of the optical isomer held before the mirror.

A model of the lactic acid molecule is shown held before a mirror (Fig. 37.8). The carbon atom held in the thumb and forefinger is asymmetric. The mirror image is another arrangement, the only other possible arrangement of

the four groups. Both compounds were in the acid from sour milk. One compound is the acid extracted from muscles. Different compounds whose structures are mirror images of one another are called *enantiomers*.



Figure 37.8. Structures of the enantiomers of lactic acid.

### C. PHYSICAL PROPERTIES OF ISOMERS

It is now obvious that the two isomers of lactic acid and, in fact, any pair of enantiomers, must have the same physical and chemical properties. It should, also, be apparent that if a solution of one enantiomer rotates light clockwise (+), a solution of the other will rotate light equally and counter-clockwise (—).

### D. FORMULAS AND NOMENCLATURE OF ISOMERS

Because organic compounds are three dimensional, and because the asymmetry of optical isomers is not apparent from a two dimensional formula, a convention must be adopted to indicate this third dimension.

When writing or observing structural formulas, the asymmetric carbon, assumed to be a tetrahedron, is written so that one edge is forward and



horizontal, with another edge behind and vertical. The asymmetric carbon occupies the central position (the tetrahedron) with groups above, below, to the right and to the left. The horizontal groups (those to right and left) occupy the forward edge and are in a plane above the paper, whereas the vertical groups reside in the same plane as the paper. To illustrate this, the formula for lactic acid is shown in Figure 37.9. The formula shown in Figure 37.9a has the structure represented by the tetrahedron (Fig. 37.9b).

Figure 37.9c and d represent one and the same molecule, the enantiomer of the molecule represented in Figure 37.9a and b. Other compounds having one asymmetric carbon may be compared to lactic acid if their structure is written on the page in the same way. It should be obvious that in rewriting the formulas one must be careful to check their identity or non-identity. Since horizontal groups are forward, one must rotate them a full  $180^\circ$  to test superimposability; two molecules are superimposable if like groups can be shown to occupy identical positions in space when the molecules are compared.

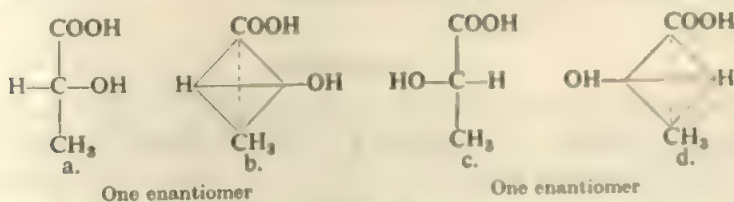
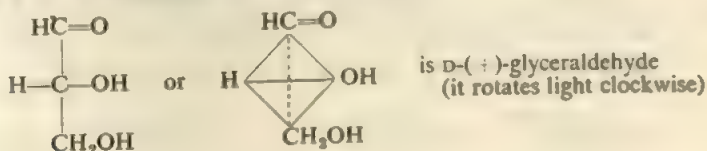
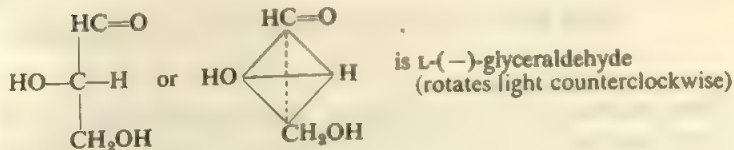


Figure 37.9. Enantiomers of lactic acid.

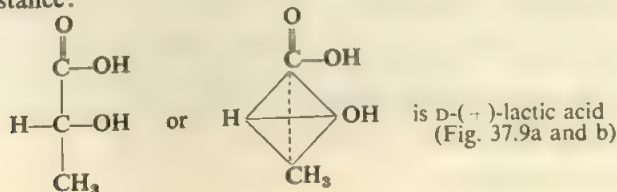
In naming optically active compounds, the direction of optical rotation is signified by a (+) or a (−), for clockwise and counterclockwise, respectively. A capital D- or L- is used to indicate that the molecule is related in structure to either D- or L-glyceraldehyde. For example:



whereas

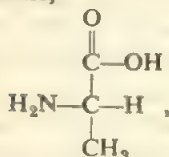


The substance:



It is the lactic acid found in muscle extract and has a (+) rotation. It is D-lactic acid, for it can be formed from D-glyceraldehyde. L-Glyceraldehyde, the other enantiomer, yields L-lactic acid. Each transformation involves several steps.

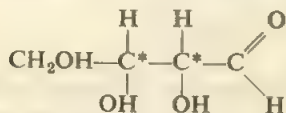
L-Alanine,



is related to L-glyceraldehyde and L-lactic acid. The name as written does not reveal the direction of optical rotation. The rotation of L-alanine is  $+14.5^\circ$  (in 6 N HCl). The complete name would be L-(+)-alanine. Note that the D- or L- prefix does not specify the direction of rotation, but only the structural similarity to D- or L-glyceraldehyde.

### E. DIASTERIOMERS

A molecule may possess several asymmetric carbons. The four-carbon sugars are examples of compounds with two asymmetric carbons. The optical isomers all have common names but all are: 2,3,4-trihydroxybutanal.



There are four optical isomers (all known) as illustrated in Figure 37.10.

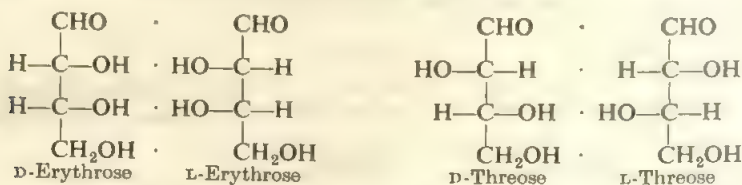


Figure 37.10. The optical (stereoisomers) of 2,3,4-trihydroxybutanal.

There are two pairs of enantiomers. D-threose and L-threose are mirror images and have the same physical properties. They rotate light equally, but in opposite directions. D-erythrose and L-erythrose are mirror images; they have the same physical and chemical properties and rotate light equally, but in opposite directions. An erythrose and a threose, however, are not mirror images, nor do they have identical properties. They are called *diastereomers*. They are optical isomers, but not enantiomers.

\* Asymmetric carbon atoms.

## F. SYNTHESIS OF OPTICALLY ACTIVE COMPOUNDS

A 50:50 mixture of enantiomers, such as obtained by Scheele when he isolated lactic acid from sour milk, is called a *racemic mixture*. Ordinary chemical syntheses of optically active compounds yield racemic mixtures. Only in special cases can one start with an optically active pure substance and prepare another without destroying the optical rotation. *Biosynthesis* (synthesis by living organisms) is usually stereospecific, leading to the formation of one or the other of the enantiomers, but not both.

## EXERCISES

- Define each and illustrate with an example each starred (\*) term.
 

a. *isomers	h. *diastereomers
b. *functional isomers	i. *asymmetric carbon
c. *chain isomers	j. *enantiomers
d. *geometrical isomers	k. *racemic mixture
e. *steriomers	l. optical rotation
f. optical isomers	m. plane polarized light
g. optically active isomers	
- Compare the properties of:
  - a pair of chain isomers
  - a pair of functional isomers
  - a pair of geometrical isomers
  - a pair of enantiomers
  - a pair of diastereomers
- Write the proper projection formula for D-2-hydroxypropanal.
- Which of these compounds are optically active: (a) 2-butene, (b) chlorohydroxymethanol, (c) 2,3-dihydroxybutanediol, (d) 1-chloro-2-hydroxyethane, (e) 1-chloro-2-hydroxypropane?
- Draw projection formulas for and name all isomers of 2,3-dihydroxybutanoic acid. Identify all pairs of enantiomers and all pairs of diastereomers.
- How many isomers are there with the formula  $C_4H_{10}$  (do not forget possible ring compounds)? Name each isomer.
- Remembering functional groups, name a pair of cis-trans isomers which will differ as greatly in properties as maleic acid and fumaric acid.
- Contrast glycerol and  $CH_2OHCHOHCH_2Br$  with respect to the number of optical isomers.

## AMINO ACIDS; PEPTIDES; PROTEINS

The name protein is a term applied to a widely distributed class of natural polymers noted particularly for their unique association with living things. In fact, the only known sources of protein materials are living organisms. Proteins make up the bulk of the solid matter of all living cells, and for these units of living matter they serve either as functional participants in the many activities which take place, or as components of the structural framework. Proteins chemically are very complex substances. Their study presents the chemist with many difficulties because of their extreme sensitivity to heat and chemical reagents.

Amino acids and peptides are simple, nitrogen-containing compounds obtained by the hydrolysis of proteins. Since their structures are relatively simple and because their reactions are more easily understood, we shall begin this study by examining first the structure and behavior of the alpha amino acids, fundamental building blocks from which all proteins are constructed. The simpler compounds of the amino acids, the peptides, will then be discussed, after which proteins will be considered.

### 1. AMINO ACIDS

#### A. GENERAL ASPECTS

An amino acid, as the name implies, is a difunctional compound which contains both an amino and an acidic group. The acid group may be one of several types, the most commonly encountered being the carboxyl. Amino sulfonic acids are known, but they are encountered less frequently. Several biologically important amino acids which serve to illustrate the various types of known amino acids are given in Figure 38.1.



Taurine is an amino sulfonic acid. Alanine is an amino carboxylic acid. More specifically, alanine is an example of an alpha amino acid, a distinction based on terminology which designates the carbon next to a carboxyl group as an alpha carbon atom. The  $\beta$ - in  $\beta$ -alanine, an amino acid found in nature, signifies that the amino group of the molecule is attached to a carbon located

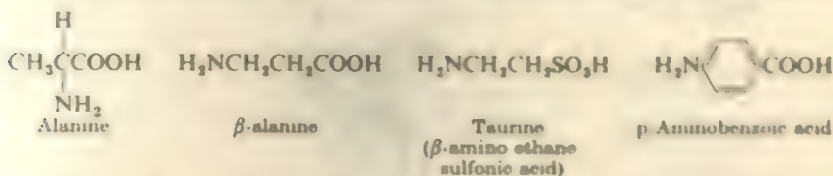


Figure 38.1. Types of amino acids.

in a beta position with respect to the carboxyl group. Alanine and  $\beta$ -alanine are structural isomers. Para-aminobenzoic acid is an example of an aromatic amino acid. Formerly thought to be a vitamin in its own right, p-aminobenzoic acid is now recognized to be important, mainly because it is a component of another vitamin, folic acid.

All but two of the acids which have been isolated from protein hydrolysates are  $\alpha$ -amino acids. Two imino acids, proline and hydroxyproline, which are

$$\begin{array}{c} \text{H} \\ | \\ \text{—N—} \end{array}$$

secondary amines having the imino ( $\text{—N—}$ ) group, have also been obtained from protein hydrolysates. They are not true alpha amino acids, since the nitrogen present is tied up in a cyclic structure. The formulas for proline and hydroxyproline are given in Table 38.1. Table 38.1 gives the names, formulas and different classifications for 20 amino acids whose presence in proteins has been verified repeatedly through isolation from protein hydrolysates. It should be noted that the names given are the common names. These will be used in this chapter, since they are more widely employed than are the systematic official names. This means that a certain number of them will have to be committed to memory. The starred amino acids are those commonly designated as the essential amino acids. Essential amino acids are no more essential to the animal body than other amino acids, but they are not manufactured by animal organisms and therefore must be provided in the diet.

The general formula used for  $\alpha$ -amino acids is:

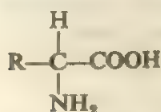


Figure 38.2 shows the model of a simple amino acid, alanine, with each atom labelled to show more clearly the actual structure.

Examination of this structure shows that in alanine, as in all  $\alpha$ -amino acids, both a carboxyl group and an amino group are attached to the same carbon. Differences which become apparent when one studies the chemistry of the individual amino acids must therefore be the result of a variation in the

structure of the R group present. The properties characteristic of particular amino acids are determined largely by the nature of this group. The R— is sometimes referred to as the side chain of the amino acid.

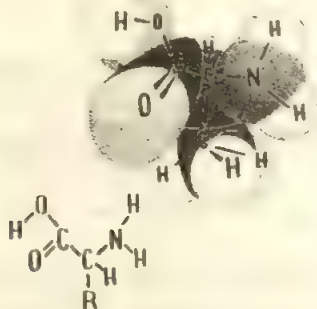


Figure 38.2. Alanine.

### B. CLASSIFICATION OF AMINO ACIDS

Depending on the type of R group, amino acids may be classified in various ways. For example, if the R (side chain) is a hydrocarbon group, as is the case for alanine or phenylalanine, the amino acid will contain one basic group (the amino group) and one acidic group (the carboxyl group). Amino acids of this type are classified as neutral amino acids. Should the side chain itself contain a carboxyl group, as is true for aspartic and glutamic acids, the amino acid will have two carboxyl groups and only one amino group. It is then referred to as an acidic amino acid. On the other hand, if the radical carries a basic group, the number of basic groups present will be larger than the number of acidic groups. Acids of this type are known as basic amino acids.

Other terms are used at times to help clarify further the structural features of the R— group. If the radical is an alkyl group, the acid is an aliphatic amino acid. When a benzene ring is part of the side chain, the compound is considered to be an aromatic amino acid. Others are designated as heterocyclic amino acids to specify the presence of a cyclic structure in which atoms other than carbon are part of the ring. Proline is an example of one of these. Amino acids containing hydroxyl groups or sulfur atoms are often designated as hydroxyl-containing or sulfur-containing amino acids. The various classifications into which the different amino acids fit are given in Table 38.1.

### C. PROPERTIES OF AMINO ACIDS

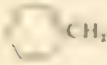
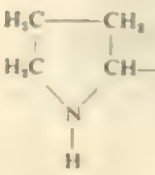

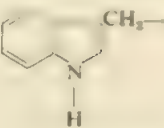
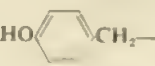
Some of the physical properties of amino acids differ rather noticeably from those one usually associates with organic compounds. For example, amino acids melt at relatively high temperatures (often above 250°). Decomposition usually accompanies the melting. Likewise, the majority of the amino acids are more soluble in water than in typical organic solvents. As a matter of

Table 38.1. Protein Amino Acids

Amino Acid	Structural Formula (R group)	Classification
Alanine	$\text{CH}_3-$	Neutral, aliphatic
Arginine*	$\begin{array}{c} \text{NH} \\   \\ \text{H}_2\text{NCNHCH}_2\text{CH}_2\text{CH}_2- \end{array}$	Basic, aliphatic
Aspartic acid	$\text{HOOCCH}_2-$	Acidic, aliphatic
Cysteine	$\text{HSCH}_2-$	Neutral, aliphatic, sulfur-containing
Cystine	$\begin{array}{c} \text{SCH}_2- \\   \\ \text{SCH}_2- \end{array}$	Neutral, aliphatic, sulfur-containing
Glutamic acid	$\text{HOOCCH}_2\text{CH}_2-$	Acidic, aliphatic
Glycine	$\text{H}-$	Neutral, aliphatic
Histidine*	$\begin{array}{c} \text{HC} \quad \text{C} \quad \text{CH}_2- \\   \quad \quad   \\ \text{N} \quad \quad \text{NH} \\ \diagdown \quad \diagup \\ \text{C} \\   \\ \text{H} \end{array}$	Basic, heterocyclic
Hydroxyllysine	$\begin{array}{c} \text{H}_2\text{NCH}_2\text{CHCH}_2\text{CH}_2- \\   \\ \text{OH} \end{array}$	Basic, aliphatic, hydroxyl-containing
Hydroxyproline	$\begin{array}{c} \text{HOCH}_2-\text{CH}_2 \\   \quad \quad   \\ \text{CH}_2 \quad \text{CH}- \\ \diagdown \quad \diagup \\ \text{N} \\   \\ \text{H} \end{array}$	Neutral, imino, heterocyclic, hydroxyl-containing
Isoleucine*	$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2-$	Neutral, aliphatic
Leucine*	$(\text{CH}_3)_2\text{CHCH}_2-$	Neutral, aliphatic
Lysine*	$\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$	Basic, aliphatic
Methionine*	$\text{CH}_3\text{SCH}_2\text{CH}_2-$	Neutral, aliphatic, sulfur-containing

\* Essential amino acids.

Table 38.1. Protein Amino Acids (Continued)

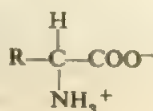
Amino Acid	Structural Formula (R group)	Classification
Phenylalanine*		Neutral, aromatic
Proline		Neutral, imino heterocyclic
Serine	$\text{HOCH}_2-$	Neutral, aliphatic, hydroxy-containing
Threonine*		Neutral, aliphatic hydroxyl-containing
Tryptophan*		Neutral, aromatic heterocyclic
Tyrosine		Neutral, aromatic, phenolic
Valine*	$(\text{CH}_3)_2\text{CH}-$	Neutral, aliphatic

\* Essential amino acids.

fact, organic solvents may be added to a water solution of amino acids to precipitate the acids present.

Observations such as these have led investigators to predict and subsequently to verify experimentally the fact that amino acids are present in solution as dipolar ions. It appears that dipolar ions are present in crystals of the solid amino acids as well.

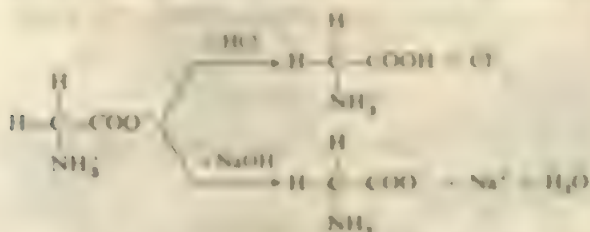
The formation of dipolar ions, in the case of amino acids, is readily explained by assuming an internal neutralization achieved by the shift of a proton from the carboxyl (a proton donor group) to the amino group (a proton acceptor). The structure formed as a result of this transformation is the dipolar ion, with its negative carboxylate and positively charged ammonium group.





In water solutions of monamino monocarboxylic acids, such as glycine or alanine, the dipolar ion may be considered as being electrically neutral, since the number of positive charges present is essentially equal to the number of negative charges. In this condition the molecule is said to be *isoelectric*.

Amino acids are said to be *amphoteric*. You will recall that this term is used to describe compounds which react both as acids and bases. The reactions of glycine with hydrochloric acid and sodium hydroxide are



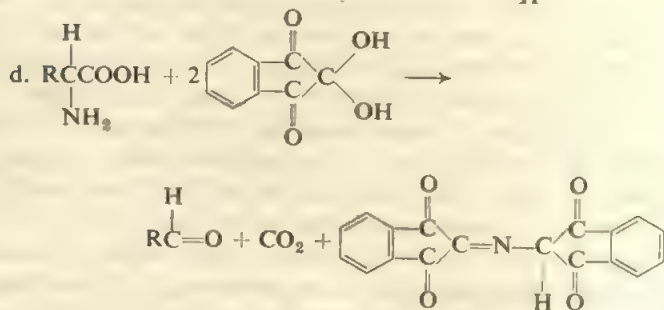
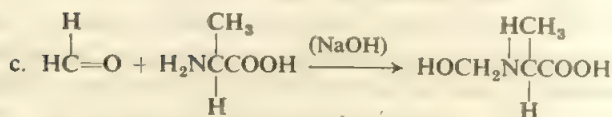
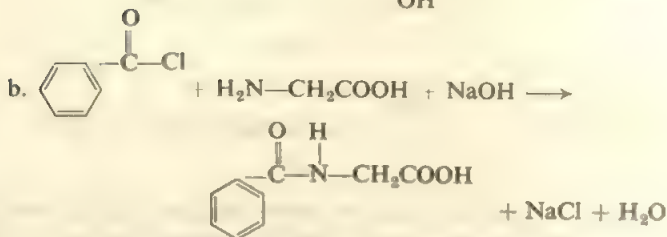
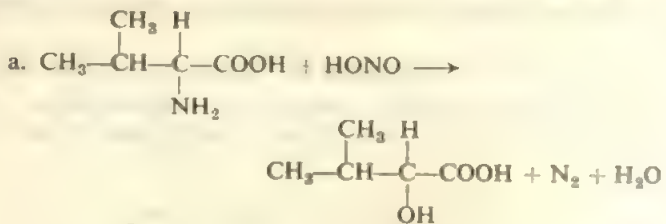
Examination of these two reactions shows that in a highly basic solution (high pH) the amino acid assumes a negative charge, whereas in a strongly acidic solution (low pH), the acid has only a positive charge. Thus it is apparent that the electrical character of the amino acid molecule in the solution is dependent upon the acidity or pH of the solution. If the amino acid solution is placed in an electrolysis cell, the amino acid molecules migrate either to the positive pole (anode) of the cell or to the negative pole (cathode), depending upon the charge. At low pH's the amino acid seeks the cathode, whereas in high pH's it moves to the anode. The pH at which the molecule is dipolar and does not migrate in the electrical field is called the *isoelectric point*. The isoelectric point is a characteristic property of each amino acid, and since the acid and basic groups present are not necessarily of equal strength, this point is usually not at pH 7. For basic amino acids, the isoelectric points are at pH's above 7. The isoelectric points for acidic amino acids will be in solutions of pH less than 7. For others the isoelectric point is near neutrality but at pH's slightly less than 7.

#### D. REACTIONS OF AMINO ACIDS

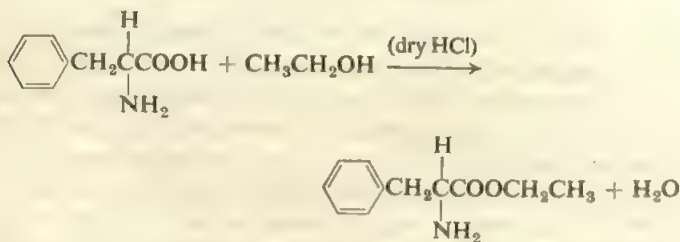
Reactions of amino acids may be grouped in two categories: (1) those which all amino acids undergo and (2) those which are peculiar to individual amino acids. For example, all amino acids show reactions attributable to the presence of carboxyl or amino groups. Tyrosine, on the other hand, while showing reactions expected for carboxyl and amino groups, in addition exhibits certain reactions characteristic of phenols, since the aromatic ring of the side chain has a phenolic hydroxyl attached to it. Cysteine, the only amino acid with a free —SH (sulfhydryl) group, undergoes a series of reactions attributable to this group.

The reactions of amino acids with acids and bases were discussed in the previous section (see above). The amino group is responsible for the

reactions which take place between amino acids and nitrous acid, acylating reagents, such as benzoyl chloride, formaldehyde and ninhydrin. Equations for the reactions of particular amino acids with these reagents are:



Esterification illustrates a type of reaction for which the carboxyl group is responsible.



The special reactions which individual amino acids show will not be discussed at this point. They will, however, be alluded to in the discussion of color tests for the presence of particular amino acids in proteins.

## 2. PEPTIDES

Peptides are condensation products of amino acids. Structurally they occupy an intermediate position between the relatively simple  $\alpha$ -amino acids and the considerably more complex proteins. The formation of a peptide by condensation is shown in Figure 38.3a and b.

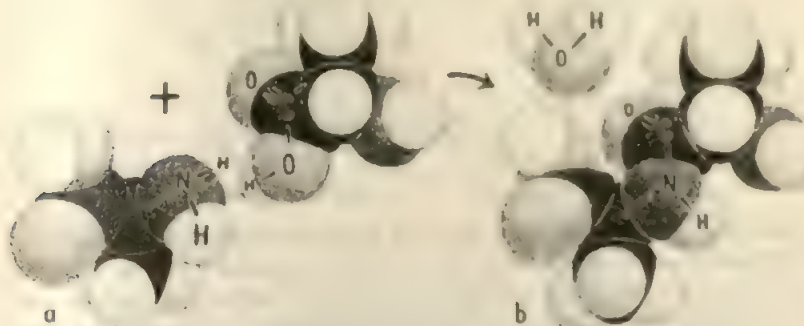


Figure 38.3. Peptide formation.

If two amino acids condense (eliminate a molecule of water) between the carboxyl group of one acid and the amino radical of the other, a substituted amide of a particular type, commonly referred to as a "peptide" is formed (Fig. 38.4). More precisely, a two amino acid peptide of this kind is designated as a "dipeptide," whereas the amide linkage ( $-\text{CO}-\text{NH}-$ ) which serves to bond together the two  $\alpha$ -amino acids in Figure 38.4 is called a "peptide bond." The constituent amino acids of peptides and proteins are linked to each other through peptide bonds.

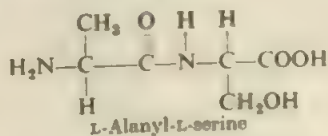
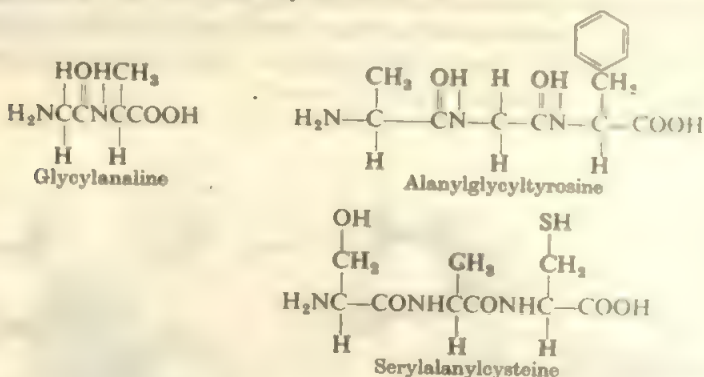


Figure 38.4. A "dipeptide."

A three amino acid peptide is called a "tripeptide," a four amino acid compound, a "tetrapeptide," and so on. Compounds in which a large number of amino acids are linked to each other through peptide bonds are known as "polypeptides." Proteins are polypeptides having very high molecular weights which range from about 10,000 to many millions. Polypeptides with molecular weights less than 10,000 are considerably more stable than proteins and usually do not undergo so readily the degradation, or changes, in physical properties which are so easily induced in proteins by heat and chemical reagents.

To form the name of a peptide, give the names of the constituent amino acids in the order they appear in the molecule. The endings of all (except the

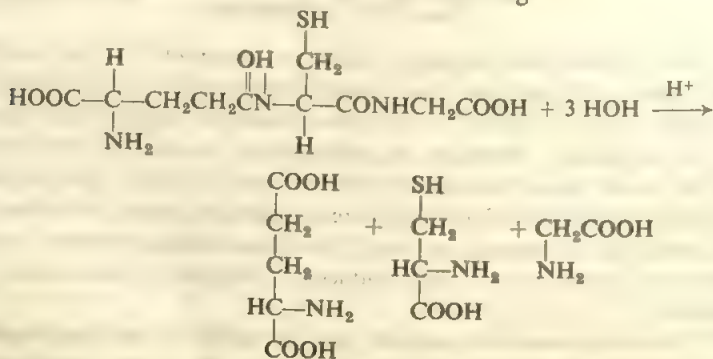
amino acid with the free terminal carboxyl group) are changed from *ine* to *yl*. Typical peptides named in this way are:



Glutathione, a peptide which occurs in nearly all living cells, has the name  $\gamma$ -L-glutamyl-L-cysteinylglycine. The  $\gamma$ -notation signifies that the glutamic acid is linked through its  $\gamma$ -carboxyl group to the amino group of cysteine.

Peptides of various types are widely distributed in nature. Some of them are characterized by the presence of rather unusual amino acids. For example, the D-isomer of phenylalanine is found to be a constituent of certain peptides with antibiotic properties. An amino acid not found in proteins, L-ornithine, the five carbon analog of lysine, is obtained from certain natural peptides. Gramicidin S, a cyclic decapeptide containing five different amino acids, contains both D-phenylalanine and L-ornithine, along with L-valine, L-leucine and L-proline,  $\alpha$ -amino acids commonly found in proteins. L-ornithine is much better known for its important role as a catalyst in connection with the formation of urea in the liver of mammals.

Hydrolysis is the most characteristic reaction of peptides. Hydrolysis amounts to the introduction of the elements of water between the carbon and nitrogen of the peptide linkage to liberate a free carboxyl and a free amino group. Complete hydrolysis of a peptide results in the liberation of all its constituent amino acids. The kinds and amounts of each kind of amino acid can then be determined by suitable analytical procedures now available. The hydrolysis of glutathione is shown in the following.





## 3. PROTEINS

## A. COMPOSITION AND CLASSIFICATION

As pointed out earlier in this chapter, proteins are polymers of amino acids. More specific structural studies have shown them to be high molecular weight polypeptides, which, because of their giant size, possess certain unique properties. Figure 38.5a and b shows a portion of a typical protein molecule.

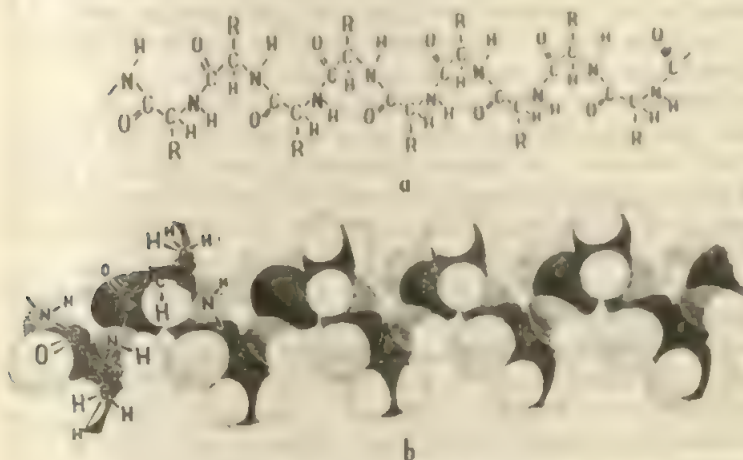


Figure 38.5. Protein fragment.

In terms of elementary composition, proteins contain all the elements found in the various amino acids: carbon, hydrogen, oxygen, nitrogen and sulfur. Smaller amounts of other elements, such as phosphorus, and certain metals, such as iron, may be present. There is no known limitation to the variety of elements. Nitrogen, however, is considered to be the characteristic element, and its average percentage composition in proteins is about 16%.

Concerning the amino acid composition of proteins, it was pointed out in the section on amino acids that some 20 amino acids have been obtained from proteins. The variety of amino acids in any one protein may be large and will sometimes consist of most, if not all, of these 20. Casein, the milk protein, is an example of a polypeptide containing most of the common amino acids. In other proteins, however, a few amino acids may make up the bulk of the constituent amino acids. For example, about 50% of the amino acid molecules liberated when silk fibroin is hydrolyzed is glycine. Keratin is another example of a protein in which a single amino acid makes up a rather large share of the units. Cystine comprises about 14% of the amino acid residues.

Several not entirely satisfactory methods are used to classify proteins. On the basis of gross structure, proteins are divided into *fibrous* and *globular* proteins. Fibrous proteins are not soluble nor dispersible in water. Keratin

(hair), collagen (connective tissue) and silk fibroin (silk) are examples of proteins of this type. X-ray studies have shown them to consist of a more or less elongated peptide chain or group of chains.

In contrast, globular proteins are generally soluble or dispersible in water. They appear to consist of a rather compactly folded or coiled chain or of a group of such chains. Most readily crystallized proteins are of this type. Insulin, a pancreatic hormone, and hemoglobin are considered to be globular proteins.

Proteins may also be classified as *simple*, *conjugated* or *derived* proteins. If a protein when completely hydrolyzed yields only  $\alpha$ -amino acids, it is classed as a simple protein. Egg albumin (egg white) and the  $\gamma$ -globulins of blood proteins are usually considered to be simple proteins.

A conjugated protein, on the other hand, is composed of a simple protein combined with a characteristic non-amino acid substance. When the non-amino acid substance is an organic compound of some type, it is usually referred to as a "prosthetic group." Vitamins often are components of these prosthetic groups. Familiar conjugated proteins are hemoglobin, casein, tobacco mosaic virus, polio virus, enzymes and mucin.

The class of derived proteins encompasses a rather heterogeneous group of materials which form when proteins are altered by chemical or physical treatment. Coagulated egg white is an example of a substance of this type.

Solubility differences between proteins may be used to further subdivide the compounds within a given category. For example, albumins may be distinguished from globulins on this basis. Albumins are soluble in both water and salt solutions, whereas globulins are sparingly soluble in water.

For more details concerning protein classification, the student should consult a standard textbook of biochemistry.

## B. PHYSICAL PROPERTIES OF PROTEINS

The physical properties of proteins reflect their large size. Most proteins do not diffuse through membranes such as cellophane or cell walls. They exist in solution as colloidal particles and show properties associated with the colloidal state of matter. For example, despite their large size they do not settle from suspension unless placed in an ultracentrifuge and rotated at speeds producing centrifugal forces many times that of gravity.

Solid proteins are usually amorphous, although some have been obtained as crystalline solids. Being composed of optically active amino acids, they are also optically active. Their solubility varies widely, depending both upon their composition and the nature and pH of the solvent used to dissolve them. Proteins decompose at relatively low temperatures without melting, and they are very sensitive to changes in the environment. Exposure to heat or extremes of pH usually produces rather drastic nonhydrolytic changes in the structure of the protein. These changes often produce marked alterations in physical properties. Heating often leads to a marked decrease in solubility, which may result in the precipitation of the protein as a

result of its coagulation. If the action of heat, pressure, irradiation, strong acids or other chemical agents makes such a profound change in the protein that its structure cannot be restored to its original form, the protein is said to have been *denatured*. Denaturation converts certain proteins (egg albumin) which are highly resistant to digestive enzymes into products which are easily digested.

Proteins are also amphoteric in behavior, a result of the presence of free basic and free acidic groups. Most of these groups come from the acidic and basic amino acids which are components of the polypeptide chain. A free amino group will also be located at the N-terminal and a free carboxyl group at the C-terminal end of the protein chain. As with amino acids, protons shift easily from carboxyl groups to amino groups, forming negative carboxylate and positive ammonium ions. Proteins, as a result, carry many negative and positive charges and contain a large number of dipoles. This makes them highly polar.

The net charge carried by a free native protein at a certain pH depends mainly upon its amino acid composition. Should the protein contain a larger percentage of acidic than basic groups, it will be an acidic protein and usually carry a negative charge at rather high pH's. A protein which has a preponderance of basic amino acids will normally carry a positive charge even at rather low pH's and will be classed as a basic protein.

In solution, however, the charge carried by the protein will also depend upon and vary with the pH, just as the charge on an amino acid varies with the acidity of the solution. Proteins react with both acids and bases. Protons attach themselves to the negative carboxylate groups, and with bases the positive ammonium ion gives up a proton. In solutions of low pH a protein takes on a net positive charge and will migrate to the cathode in an electrolysis cell. In solutions of high pH, a protein assumes a net negative charge and migrates to the anode. At some intermediate pH value the number of negative charges in the protein will equal the number of positive charges and it will carry a net charge of zero. At this pH the protein does not migrate in an electric field. This pH is referred to as its isoelectric point. Just as the isoelectric point is a specific property of individual amino acids, it is a unique property also of individual proteins. Many properties of proteins show a minimum or maximum value at the isoelectric point. For example, most proteins are least soluble at their isoelectric point and often are least stable to heat and chemical transformation at this pH.

### C. CHEMICAL PROPERTIES AND TESTS

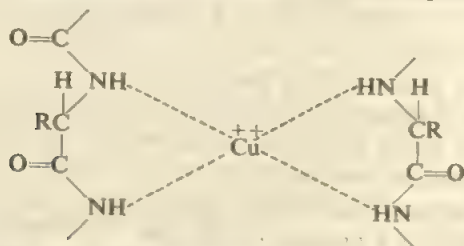
Many proteins precipitate from aqueous solution when organic solvents such as alcohol or acetone are added. This addition favors the attractive forces of adjacent protein molecules for each other, which aids their precipitation. Neutral salts are also effective in precipitating certain proteins. Ammonium sulfate is widely used in procedures used to separate proteins by selective precipitation.



Heavy metal salts of lead, mercury or copper are usually insoluble. Solutions of these ions usually precipitate proteins. The positive metal ions react with the negative charges on the protein to form the salts. Likewise, acidic reagents, such as trichloroacetic acid, react with proteins to form insoluble salts. The negative trichloroacetate ion reacts with the positive groups on the protein, forming salts which precipitate. Egg white is used as an antidote for mercury or lead poisoning because it reacts with and traps these metal ions until the stomach can be pumped to remove the metal ion containing protein.

A variety of color tests or reactions have been used in the study of proteins. The biuret test, for example, is a general reaction used to show the presence of and amount of proteins in solution. On the other hand, other tests are more specific and are used to detect certain functional groups, which, when shown to be present, are evidence for the presence of certain amino acids. Some of these tests are discussed below.

**Biuret test.** Substances containing two or more peptide linkages produce a reddish-violet color with dilute copper sulfate in strong alkali. The color is due to the formation of a complex between the cupric ion and several of the peptide bonds in the protein. This complex is shown as follows:



The biuret test is generally positive for proteins and polypeptides. It is called the biuret test because the compound biuret, formed when urea is heated, is responsible for a similar color.

**Xanthoproteic Test.** When proteins containing aromatic groups are heated with concentrated nitric acid, they turn yellow. The chemical reaction responsible for the color is the nitration of aromatic compounds. Easily nitrated aromatic compounds, such as tyrosine and tryptophan, undergo this reaction. The yellow nitro compounds formed are converted to orange colored salts by alkali. Phenylalanine does not respond. Skin stains yellow when nitric acid contacts it, because aromatic amino acid units occur in the proteins. Subsequent addition of a base turns them reddish-orange.

**Millon's Test.** Millon's reagent, which is a mixture of mercuric and mercurous nitrates in concentrated nitric acid, forms a red color with compounds containing phenolic groups. Tyrosine, having a phenolic ring in its R-group, undergoes this reaction whether free or combined in protein.

**Hopkins-Cole Test.** In the presence of concentrated sulfuric acid, glyoxylic acid condenses with indole compounds to form brightly colored compounds. The phenomenon can be observed when glyoxylic acid is added to certain protein solutions and concentrated sulfuric acid is poured slowly down the container so that it forms a layer on the bottom. If indole is present in the



protein, a violet ring is formed at the interface between the two solutions. This test is specific for the presence of tryptophan in proteins since tryptophan is the only amino acid having an indole ring.

**Nitroprusside reaction.** The presence of free sulphydryl groups is shown by the formation of a red color when sodium nitroprusside in an ammoniacal solution is added to a solution of a compound. Proteins that give a red coloration on addition of ammoniacal sodium nitroprusside solution contain cysteine units with its free sulphydryl groups.

#### D. BIOLOGICAL SIGNIFICANCE OF PROTEINS

The ability to synthesize proteins is a unique characteristic of living organisms. Proteins are intimately connected with almost all the chemical and physical activities that constitute life; in fact, there is hardly an important physiological function in which proteins do not participate.

Some proteins, called enzymes, serve as catalysts to speed up the variety of chemical transformations which living cells are able to accomplish. Other proteins function as hormones whose principal activity is to control processes which occur in living things. The growth hormone produced by the pituitary gland is an example of such a hormone. Likewise, hemoglobin, a protein in the blood, serves as an oxygen carrier to transport oxygen from the lungs to the various tissues. Still another protein, actomyosin, participates in muscular contraction. Nucleoproteins, typical conjugated proteins, composed of substances called nucleic acids combined with simple proteins, are the main constituents of genes, the carriers of heredity. In addition, antibodies, which are proteins produced in response to the introduction of foreign proteins into the blood, function to protect man against disease. Less spectacular are the proteins such as hair and fingernails which serve as important structural elements of the body.

Finally, it should be pointed out that the structures of proteins are highly specific. Those made by living organisms are composed of L-amino acids, that is, amino acids related in their configuration to L-glyceraldehyde, discussed in the previous chapter. This contrasts markedly with the carbohydrates (see the next chapter), which are related in their structure to the compound D-glyceraldehyde.

#### EXERCISES

1. Define:

- a. amino acid
- b.  $\alpha$ -amino acid
- c. dipeptide
- d. polypeptide
- e. peptide bond
- f. acidic amino acids
- g. difunctional compounds
- h. condensation product
- i. hydrolysates
- j. essential amino acids
- k. aromatic amino acids

- l. isoelectric point
- m. amphoteric
- n. cathode
- o. polymer
- p. fibrous protein
- q. globular protein
- r. simple protein
- s. conjugated protein
- t. derived protein
- u. denaturation

2. What elements are invariably found in proteins? What other elements are sometimes found in proteins?
3. Explain, using structural formulas, the existence of amino acids in solution as dipolar ions. Show how an amino acid in solution may be given either a positive or a negative charge by changing the pH.
4. Compare the physical properties of fats and proteins.
5. Write equations showing special conditions and catalysts for the reaction of glycine with: (a) acetyl chloride, (b) formaldehyde, (c) ethyl alcohol.
6. Write an equation for the hydrolyses of the tripeptide of alanine.
7. Give the reagent(s), the procedure, and the observation necessary for a positive test and the group detected by the:
  - a. biuret test
  - b. xanthoproteic test
  - c. Millon's test
  - d. Hopkins-Cole test
  - e. nitroprusside reaction

## CARBOHYDRATES

The term carbohydrate is used to identify a rather diverse group of materials found in nature and known to have important functions as constituents of both plants and animals. They provide a structural framework for plants and serve as a source of energy for both plants and animals. Table sugar, wood, cotton, milk sugar, potato starch and honey are carbohydrates familiar to most of us. Chitin, the hard substance forming the shell of insects and crustacea, is a less familiar carbohydrate.

Carbohydrates, as the name implies, are composed mainly of carbon, hydrogen and oxygen, although other elements have been found in a few compounds. For example, chitin contains nitrogen. The observation that many of the simpler compounds had carbon, hydrogen and oxygen in the ratio  $\text{CH}_2\text{O}(\text{C}_n\text{H}_{2n}\text{O}_n \text{ or } \text{C}_n(\text{H}_2\text{O})_n)$  gave rise to the name carbohydrate (hydrates of carbon), although they are in no sense hydrates.

Structurally, carbohydrates are polyfunctional compounds. They contain two kinds of functional groups, the hydroxyl group and the carbonyl group. They are polyhydroxy aldehydes or ketones, or are more complex materials, which yield such aldehydes or ketones when hydrolyzed. Since the carbonyl group, due to intramolecular cyclization with a hydroxyl group, may be part of a ring structure, some carbohydrates are said to contain potential aldehyde or ketone groups.

## 1. CLASSIFICATION

The behavior of carbohydrate materials when subjected to acid hydrolysis provides the basis for an initial separation into groups. The simplest of these do not hydrolyze into smaller units. Substances of this kind are the least complex of the carbohydrates and are known as "monosaccharides."\*

\* The Greek word *sakcharon* means sugar. Saccharides is a general term for carbohydrates.

Compounds, on the other hand, which undergo hydrolysis to liberate two or more, but fewer than eleven monosaccharide molecules, are designated as "oligosaccharides." Many of these lower molecular weight carbohydrates have a sweet taste. Because of this they are often referred to as "sugars."

If more than ten molecules of monosaccharide result when hydrolysis occurs, the compound is referred to as a "polysaccharide." Thus, using this response of different carbohydrates to one type of chemical reaction as a basis, three classes of carbohydrates may be distinguished: monosaccharides, oligosaccharides and polysaccharides.

Subdivisions within each group specified here will be discussed in the section dealing with each class of carbohydrate. Structural considerations are used to make finer distinctions and a further designation is employed to show more fully the constituents of each carbohydrate.

## 2. MONOSACCHARIDES

Names most used for carbohydrates are the common names and these will be employed in this chapter. The characteristic ending used in naming monosaccharides is *ose*. This is attached to a suffix which may reflect either the source or the historical origin of the carbohydrate. Systematic names can be obtained and will be given occasionally, along with the common names, to illustrate the way in which such names for carbohydrates are formed.

### A. TYPES OF MONOSACCHARIDES

Monosaccharides are divided into subgroups on the basis of the number of carbon atoms in each molecule. A two carbon monosaccharide is referred to as a biose, a three carbon compound as a triose and one with four carbons as a tetrose. The pentoses, which have five carbons, are important constituents of viruses and related substances. Hexose refers to the six carbon monosaccharides. They are the most important monosaccharides from the standpoint of abundance and distribution in living things.

The monosaccharides, with the exception of the bioses, may be either polyhydroxy aldehydes or polyhydroxy ketones. Monosaccharides which have an aldehyde or potential aldehyde group are referred to as "aldoses". Similarly those with a keto or a potential keto group are designated as "ketoses." Within each category of monosaccharides we find both aldoses and ketoses.

Table 39.1 lists the various types of monosaccharides along with several of the more important compounds of each kind.

Examination of the table reveals several important facts. Aldoses only are listed for the biose and tetrose classifications. Only one biose, an aldehyde (glycol aldehyde), is possible. The ketotetroses are not particularly important, so they are not included in the table. It should be observed that the name of each optically active sugar listed in the table is preceded by a capital D. This notation is used to designate a structural relationship between the compound and that stereoisomer of glyceraldehyde which was assigned the



name D-glyceraldehyde. The name of a monosaccharide which can be converted into, or which can be made from, D-glyceraldehyde by suitable chemical reactions will be preceded by a capital D to show this relationship. Monosaccharides related to L-glyceraldehyde in the same way are designated with a capital L in front of their names. The relationship spoken of here is referred to as the configuration of the molecule. The optically active compounds

Table 39.1. Monosaccharides

Classification		Example	Optical Rotation [ $\alpha$ ] <sub>D</sub> <sup>20</sup>
Biose	Aldose	Glycol aldehyde	Inactive
Triose	Aldose	D-Glyceraldehyde	+21.2°
	Ketose	Dihydroxy acetone	Inactive
Tetrose	Aldose	D-Erythrose	-14.5°
		D-Threose	-12.3°
Pentose	Aldose	D-Ribose	+25.0°
		D-Arabinose	+105.1°
		D-Xylose	+18.6°
		D-Lyxose	-14.0°
	Ketose	D-Xylulose	
Hexose	Aldose	D-Glucose	+52.5°
		D-Galactose	+79.3°
		D-Mannose	+14.2°
		D-Gulose	-20.4°
		D-Allose	+14.4°
	Ketose	D-Fructose	-92.0°

listed in the table all have the D configuration. Again to emphasize the point, this relationship is structural and is not directly related to the direction of optical rotation of the compound. Optical rotation is a specific physical property whose value is determined by measurement. Only D-monosaccharides are listed, because the naturally occurring and biologically important monosaccharides are of this configuration. L-monosaccharides are rarely encountered and are relatively insignificant.

## B. THE HEXOSES

The hexoses as a class are by far the most important of the monosaccharides. Glucose is the most important hexose. Thus, glucose warrants special consideration. From a chemical standpoint, studies of the chemistry and properties of glucose have provided much of what is now known concerning the structure and behavior of carbohydrates in general. Furthermore,

glucose is the central carbohydrate of living organisms of all types, the major source of the energy which humans require for their day to day activities. It is widely distributed in nature as the monosaccharide in grape sugar and honey, as a component of the disaccharides, lactose, maltose, cellobiose and sucrose, and it is the building unit from which the polysaccharides, starch, cellulose and glycogen, are formed.

### (1) GLUCOSE

The structural formula for glucose was arrived at from a consideration of facts and conclusions such as the following:

(a) Quantitative analysis establishes the empirical formula,  $\text{CH}_2\text{O}$ . This type of formula shows only the kinds of, and ratio between, atoms present in a compound.

(b) The molecular weight of glucose, determined from a study of the freezing point of glucose solutions, shows a value of 180. When this is compared with the empirical formula weight (30), the conclusion is reached that the molecular formula is  $6(\text{CH}_2\text{O})$ , or  $\text{C}_6\text{H}_{12}\text{O}_6$ .

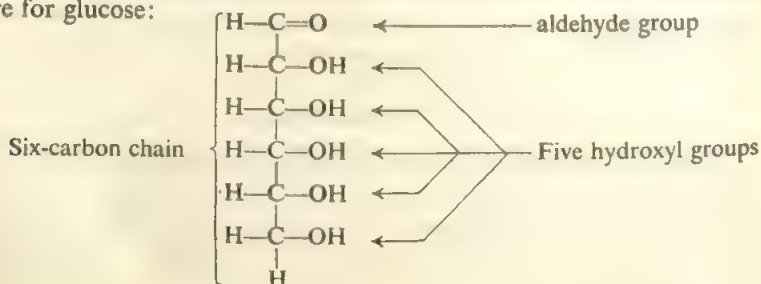
(c) Glucose, when subjected to reduction under the proper conditions, is converted into n-hexane. This is possible only if the carbon atoms of glucose are united with each other to form an open-chain of six carbon atoms.

(d) Glucose reacts readily with reagents commonly employed to show the presence of a carbonyl group (Chapter 33). For example, glucose adds  $\text{HCN}$ , reacts with hydroxyl amine and phenylhydrazine. The compounds obtained from glucose are those one would expect if an aldehyde, ( $\text{CHO}$ ) group, were present. It may be concluded therefore that glucose has an aldehyde functional group.

(e) The presence and the number of hydroxyl groups are shown by reacting glucose with acetyl chloride. Five acetyl groups are introduced into the molecule to form pentaacetyl glucose. Five hydroxyl groups are therefore assumed to be present, and since two hydroxyl groups attached to one carbon are usually unstable, it is further concluded that the five hydroxyl groups are on separate carbon atoms.

(f) Oxidation reactions are in agreement with the above facts. Mild oxidation gives a six-carbon monocarboxylic acid. This is characteristic of an aldehyde. More drastic oxidation forms a six-carbon dicarboxylic acid.

Combining these facts to design a structural formula leads to this *tentative* structure for glucose:



The formula shows this carbohydrate to be a polyhydroxy aldehyde (pp. 629, 630). Glucose, however, is optically active and further examination shows the presence of four asymmetric carbon atoms, which, if the carbonyl carbon is numbered 1, are carbons number 2, 3, 4 and 5. The presence of four asymmetric carbon atoms indicates the existence of 16 optical isomers of glucose, the number of which may be calculated from the van't Hoff rule: *The number of optical isomers =  $2^n$ , where  $n$  = the number of asymmetric carbon atoms present.*  $2^4 = 16$ , 16 have been synthesized and identified.

**Configuration of Glucose.** Since all the optical isomers of glucose have the structural features shown in the formula given above, the various isomers

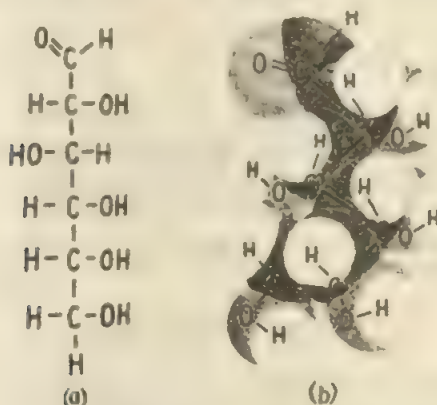


Figure 39.1. D(+)-glucose.

must differ from each other in the spatial (stereo) arrangement of the hydroxyl and hydrogen atoms about the carbons present. To establish the arrangement of the groups around each asymmetric carbon atom involves a rather lengthy and complicated series of reactions whose completion required some fifty years of study. These investigations established clearly the arrangement of the groups about these four asymmetric carbon atoms for all the predicted isomers of glucose. The structural formula assigned to glucose on the basis of these studies is shown in Figure 39.1.

This structure for glucose was firmly established with the achievement of its synthesis by Emil Fischer in 1890. Although the structure explained all the reactions known up to that time, new reactions were to be found shortly which would require an extension of this picture.

A French chemist by the name of Tanret in 1895 observed the phenomenon of mutarotation with glucose, an observation which led to the proposal and establishment of the presently accepted cyclic structure for glucose and other monosaccharides.

If ordinary D-glucose is dissolved in dilute acetic acid and allowed to crystallize, the material obtained has a specific rotation of  $+113^\circ$ . However, if another portion of this same ordinary D-glucose is dissolved in water,

acetic acid added, and the solution is heated to  $100^{\circ}$  and rapidly cooled, a crystalline material is obtained which exhibits a specific rotation of  $-19^{\circ}$ . If either of these crystalline materials is dissolved in water and allowed to stand, the specific rotation of the solution prepared changed gradually until a final value of  $+52.5^{\circ}$  is obtained. Tanret could explain this gradual change in optical rotation (mutarotation) only if there were two forms of D-glucose that could change from one to another rather easily. Each method of crystallization yields one form. Once crystals form, no reaction can occur. As soon as the glucose is dissolved, conversion can take place and an equilibrium mixture with a rotation of  $+52.5^{\circ}$  is obtained.

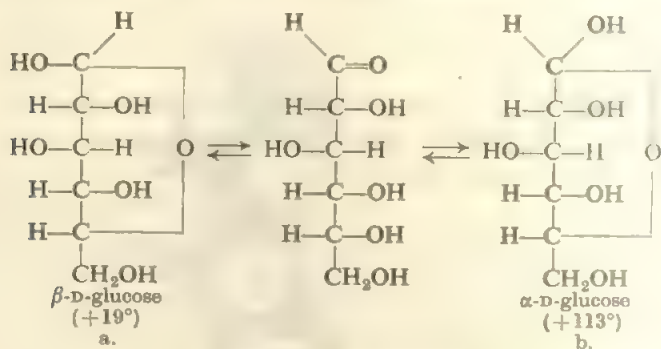
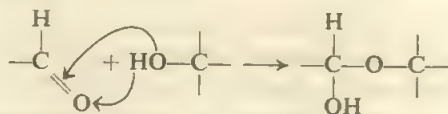


Figure 39.2. Mutarotation.

Two kinds of D-glucose can exist if the aldehyde group of the sugar were to react with an alcohol group of the same molecule to form an *intramolecular hemiacetal* (Chapter 33).



Such an intramolecular reaction would result in formation of a ring (Fig. 39.2).

Because of the alkane bond angle, which is  $109^{\circ} 28'$ , 5- or 6-membered rings are favored. With glucose the 6-membered ring is formed. Note that reaction of the OH on carbon number 5 with the aldehyde of carbon number 1 gives the 6-membered ring.

Carbon number 1 becomes asymmetric by the cyclization reaction. It is now attached to 4 different groups, making more isomers possible. This means simply that when the  $\text{—H}$  of the  $\text{—OH}$  on carbon 5 adds to the O of the planar aldehyde group, the  $\text{—OH}$  group formed may move either left or right. The left position, as indicated in Figure 39.2, gives  $\beta$ -D-glucose and the right position,  $\alpha$ -D-glucose.

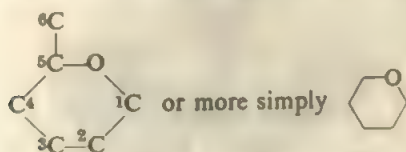
It is apparent that the cyclic glucoses (Fig. 39.2) differ from one another and that they both differ from the open chain structure in the center. All three exist in equilibrium (after mutarotation) in a solution of glucose, although only traces of the free aldehyde form are present in the mixtures.



Note that the compounds on the right and left have the OH groups situated on opposite sides of carbon 1. The isomer having the hydroxyl to the right of this carbon is designated as  $\alpha$ -D-glucose, the one having the hydroxyl on the left, as  $\beta$ -D-glucose. Because ring closure forms a fifth asymmetric carbon, each of the 16 isomers of glucose predicted using the open-chain structure, when cyclized, will form two different substances. A grand total of 32 isomers of glucose is therefore possible. Again, all are known.

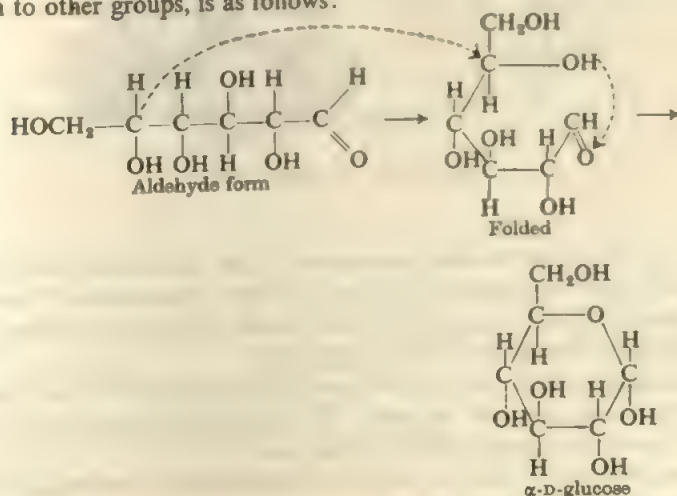
Mutarotation is now explained. The initial rotations of  $+113^\circ$  or  $+19^\circ$  are due to the presence of  $\alpha$ -D-glucose ( $+113^\circ$ ) or  $\beta$ -D-glucose ( $+19^\circ$ ), respectively. Since the two forms are interchangeable through conversion into the open chain structure, the gradual change in specific rotation is attributed to the establishment of an equilibrium between the forms. The equilibrium mixture, 37 per cent  $\alpha$ - and 63 per cent  $\beta$ -, has a specific rotation of  $+52.5^\circ$ .

The linear cyclic structures (Fig. 39.2) shown above do not accurately depict the true shape of this molecule. A formulation suggested by Haworth, in which rings are written as more or less regular hexagons, is more correct.

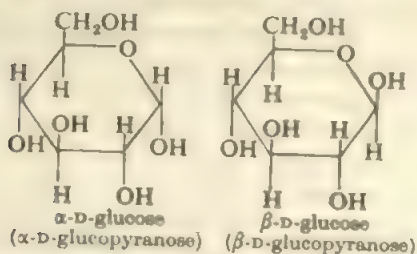


When the carbon-oxygen ring is written this way, the lower edge of this ring is assumed to be nearest the reader. Groups projecting to the right or left in the linear formula are shown as projecting above or below the plane of this ring.

The transition from the open chain to the Haworth formula, in which the open chain is first folded and the primary alcohol shown in its true steric relation to other groups, is as follows:



Using this notation,  $\alpha$ -D-glucose and  $\beta$ -D-glucose are written as:



These cyclic formulas are particularly useful for showing the structures of disaccharides and polysaccharides.

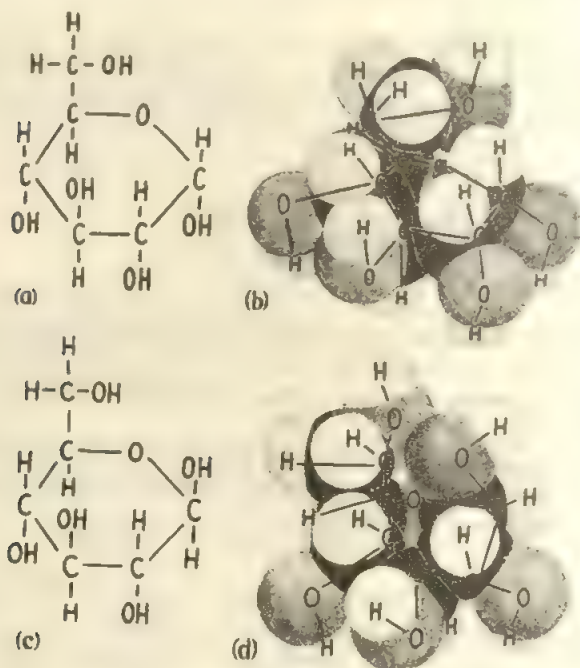


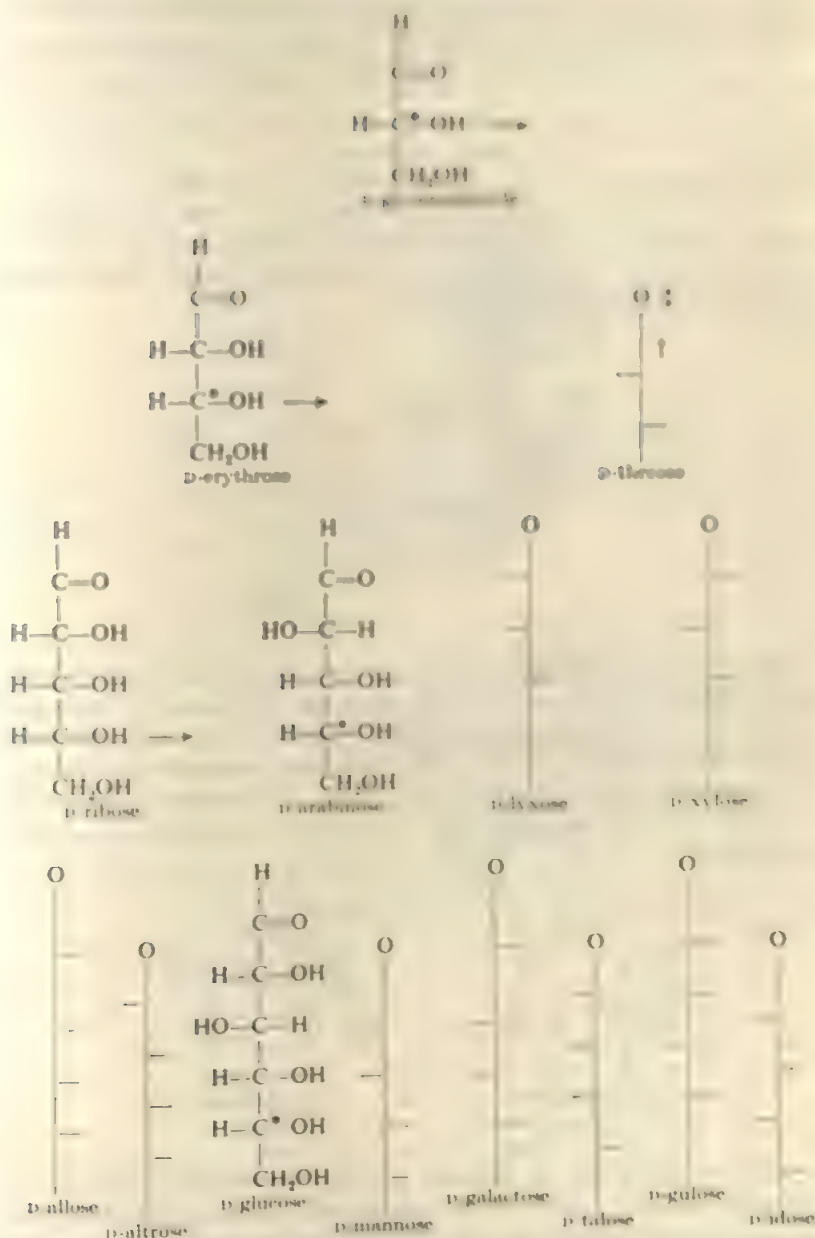
Figure 39.3. Glucose structures.

The cyclic structures usually written for  $\alpha$ - and  $\beta$ - are compared in Figure 39.3 with the three-dimensional cyclic models constructed of these same compounds, which give a more realistic picture of their actual shape. These should be compared with those in Figure 39.1.

In writing equations for the reactions of glucose, both the open chain and the cyclic structures will be used. The particular formula which appears to be the most convenient will be employed.

Table 39.2 shows the open chain structures for the optically active aldose monosaccharides in the D-series.

Table 39.2. D-Aldoses



\* Represents the D-glyceraldehyde asymmetric carbon.

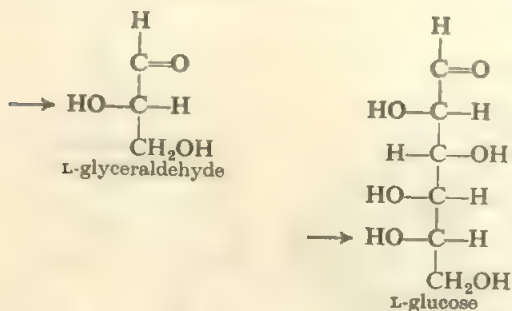
† Horizontal lines represent an —OH group.

‡ O represents the —CHO group.

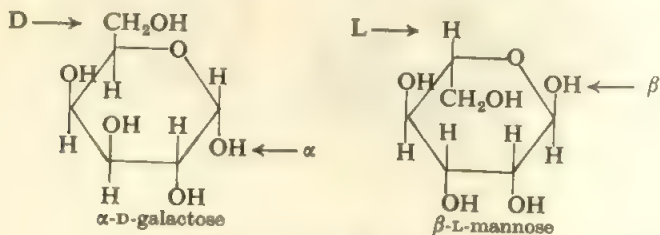
A corresponding series of L-monosaccharides could be written. For each of the monosaccharides forming cyclic structures, two isomeric compounds exist and are designated as  $\alpha$ - and  $\beta$ - forms.

The structural relationship of all D-sugars to D-glyceraldehyde is clearly seen from the table if one compares the configuration of the hydroxyl group attached to the starred carbon atom of D-glyceraldehyde with the configuration of the hydroxyl groups on the starred carbon of D-erythrose, D-arabinose and D-glucose. In each the hydroxyl is to the right.

When the aldehyde or keto group is written at the top, if the hydroxyl on this asymmetric carbon farthest from the carbonyl is to the right, the sugar is a D-sugar. If this hydroxyl is on the left, it is an L-sugar. The formulas for L-glyceraldehyde and L-glucose are:



The D-configuration is shown in the cyclic structure by the  $-\text{CH}_2\text{OH}$  being up if the ring is written with the oxygen of the ring located at the upper right as in the cyclic structure shown for glucose. For a cyclic structure written in this way, if the  $-\text{OH}$  attached to carbon 1 projects below the ring, the sugar is designated as an *alpha* sugar, if this  $-\text{OH}$  projects up (above the ring) the sugar will be a *beta* form. Formulas for  $\alpha$ -D-galactose and  $\beta$ -L-mannose are:



Glucose, also known as dextrose, is widely distributed in nature. It is used extensively as a food and sweetening agent. Large quantities are made commercially from starch each year. It is the primary carbohydrate utilized by the body tissues and is the common sugar of blood and other body fluids. It is used for intravenous feeding of medical patients unable to take nourishment in other ways. It is the sugar which appears in the blood in excessive amounts in "sugar" diabetes (diabetes mellitus).



## (2) FRUCTOSE

Fructose is the ketohexose closely related to glucose. It is the most common of the ketoses and is the monosaccharide obtained along with glucose when

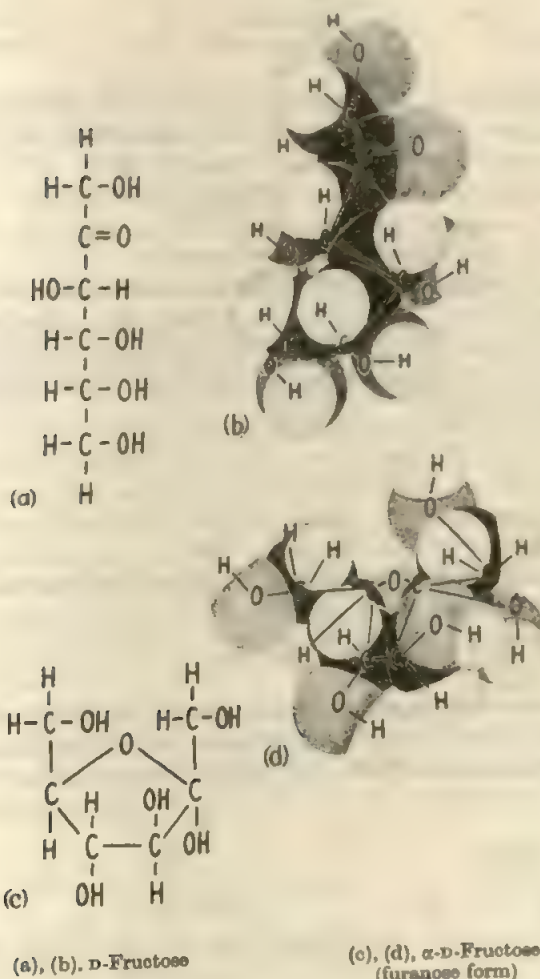
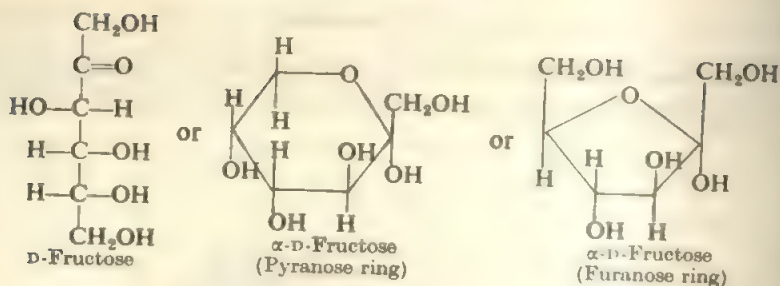


Figure 39.4. Structure of fructose.

the disaccharide, sucrose, undergoes hydrolysis. In the course of its degradation in cells and tissues glucose is converted into fructose derivatives. Fructose is sometimes given the name levulose because it rotates light to the left (levo-). Note that, although it is a levorotatory sugar, it has the D-configuration and is classed as a D-sugar. Fructose has the following structures.



The cyclic formula for fructose formed by reaction of the hydroxyl on carbon 6 with the carbonyl group gives the usual six-membered ring. However, fructose with the five-membered ring is found in nature. This results from reaction of the hydroxyl on carbon 5 with the carbonyl group.

Figure 39.4 compares the open chain and the Haworth formulas of fructose with the corresponding molecular models.

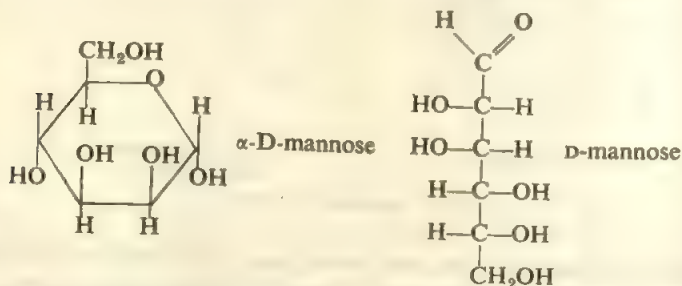
To distinguish the two types of fructose, the one with a six atom ring structure is named  $\alpha$ -D-fructopyranose, and the molecule having the five atom ring is  $\alpha$ -D-fructofuranose. Pyranose comes from the word pyran, the name for the six atom ring having five carbons and one oxygen. Furan has a ring with four carbons and one oxygen.



Note that the configurations of carbons 3, 4, 5 and 6 of fructose are exactly the same as those in glucose.

### (3) MANNOSE

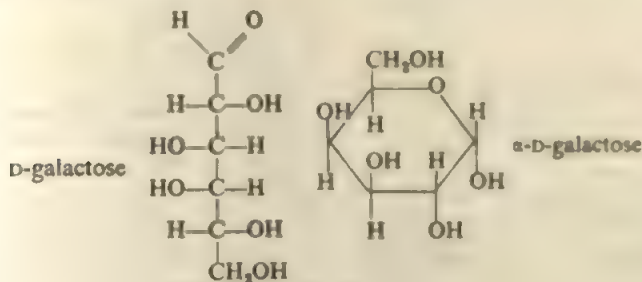
Mannose is the monosaccharide obtained from the polysaccharide mannan. It is considered here only to point up another structural relationship which exists between monosaccharides. The structure of mannose is:



An examination of the structure shows that it differs from glucose only in the configuration at carbon 2. The position of the hydroxyl on carbon 2 in mannose is the reverse of its position in D-glucose. Two sugars which differ in this way only are said to be "epimers."

## (4) GALACTOSE

Galactose is important since it is a component of the disaccharide, lactose (milk sugar). It is also a constituent of the fatty substances of brain and nerve tissue. It has the structure

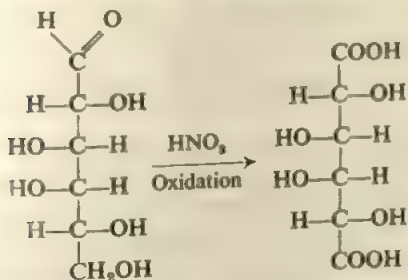


## C. REACTIONS OF MONOSACCHARIDES

Monosaccharides, because of their polyfunctional nature, can be expected to show reactions of aldehydes, ketones or alcohols.

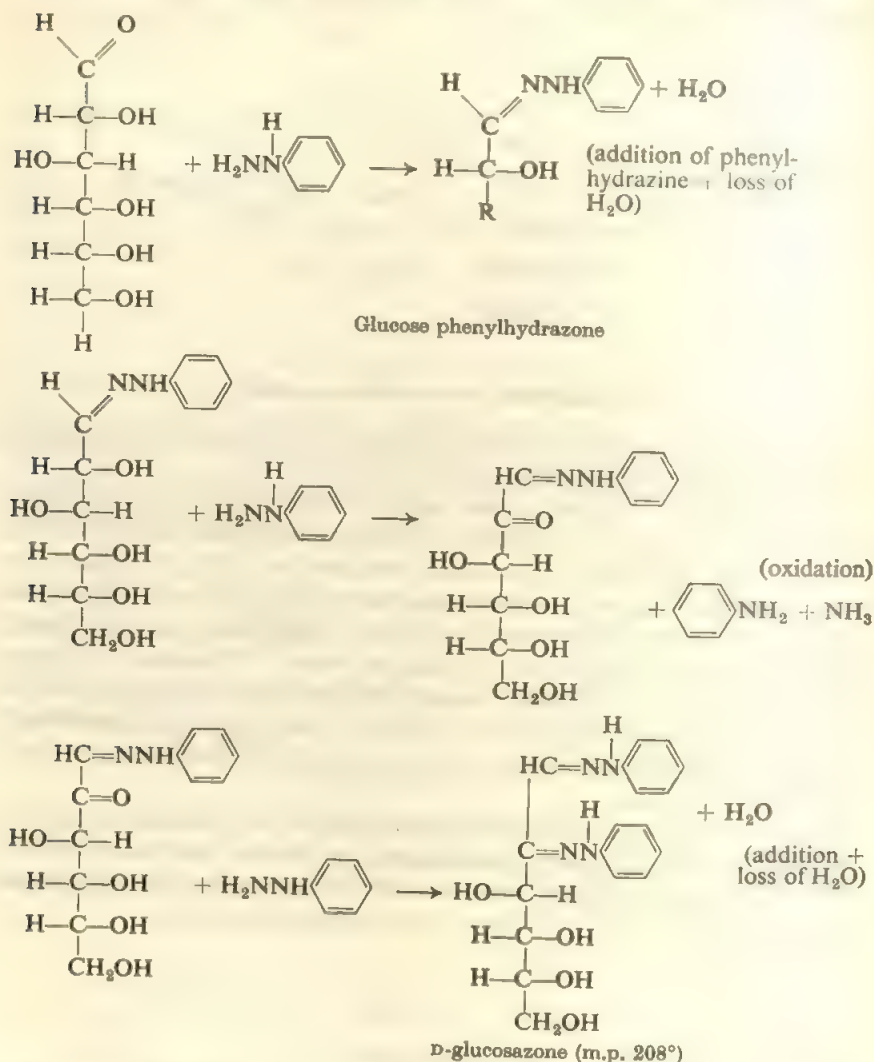
(1) **Oxidation.** Monosaccharides generally are oxidized very readily by such mild oxidizing agents as Tollens', Fehling's and Benedict's reagents. All monosaccharides, whether open-chain structures or cyclic structures, are easily oxidized. The free hydroxyl group attached to carbon 1 in the cyclic form activates the molecule toward oxidation. Sugars which react with mild oxidizing agents are referred to as "reducing sugars." Products of the reaction with Benedict's or Fehling's solution (Chapter 33) are red cuprous oxide and the monocarboxylic acid of the aldehyde. Glucose gives D-gluconic acid and red cuprous oxide. Conversion of the aldehyde of glucose into a carboxyl yields D-gluconic acid.

Nitric acid oxidizes aldohexoses to saccharic acids. Saccharic acids are terminal dicarboxylic acids. D-galactose and lactose (see next section) yields the saccharic acid, mucic acid. It is an insoluble crystalline compound and its formation is used to indicate the presence of galactose.



(2) **Osazone formation.** Phenylhydrazine reacts with aldoses to form phenylhydrazones (Chapter 33), which then react further to finally give

compounds referred to as phenylosazones. Osazones are usually easily crystallized and may be used to show the presence of particular sugars because of the characteristic crystals which appear. The sequence of reactions for glucose may be written as follows:

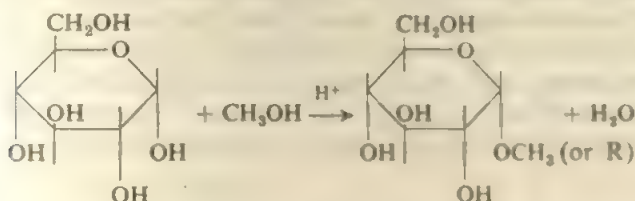


Examination of this sequence of reactions shows that only the top two carbons (carbons 1 and 2) of the monosaccharide take part in this reaction. The rest of the glucose molecule remains unchanged. This observation was of considerable significance in arriving at the structures of the isomers of glucose. Fischer found that D-mannose and D-fructose both gave the same osazone as did D-glucose. From this he concluded correctly that the arrangement of the atoms around carbons 3, 4, 5 and 6 of these three were the same.

Examine the structures of these sugars given in Table 39.2 to verify this.



(3) **Glycoside formation.** The formation of mixed acetals by the interaction of monosaccharides with alcohols in the presence of traces of mineral acids is a significant reaction. The reaction of glucose with methanol is:



Observe that this reaction takes place between the hydroxyl attached to carbon 1 of glucose (the hemiacetal hydroxyl) and that the hydrogen of the hydroxyl is replaced with a methyl group. Derivatives of carbohydrates formed when hydrogens of this kind are replaced with R groups are referred to as *glycosides*, and the bond between the radical and the monosaccharide is called a *glycoside linkage*. A compound obtained from glucose would be designated more specifically as a glucoside because it is a derivative of glucose. In this instance, it is a methyl glucoside, and, more specifically, a methyl  $\alpha$ -D-glucoside. If the methanol reacted with  $\beta$ -D-glucose, methyl  $\beta$ -D-glucoside would be obtained. Both alpha and beta glucosides are found in nature.

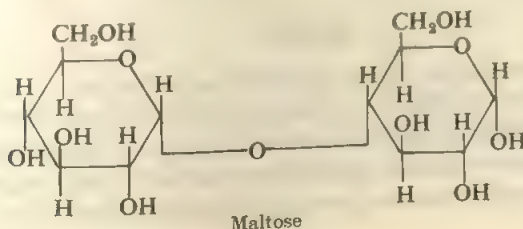
This type of combination is of interest because the disaccharides to be discussed next are joined to each other through glycoside linkages of this type. Disaccharides are glycosides in which the R group is another monosaccharide.

### 3. OLIGOSACCHARIDES

The most common and most important oligosaccharides are the disaccharides. Disaccharides are all glycosides of a particular kind in which the R— group is another monosaccharide. Four of these will be discussed: maltose, cellobiose, lactose and sucrose. Of these, sucrose is the most common.

#### A. MALTOSE

Maltose hydrolyzes to yield only glucose. Structurally it is a glucoside in which the R group is another glucose molecule. It consists of two glucose units joined together by an alpha-glucosidic linkage between carbon 1 of one unit and carbon 4 of another. Its structure is:

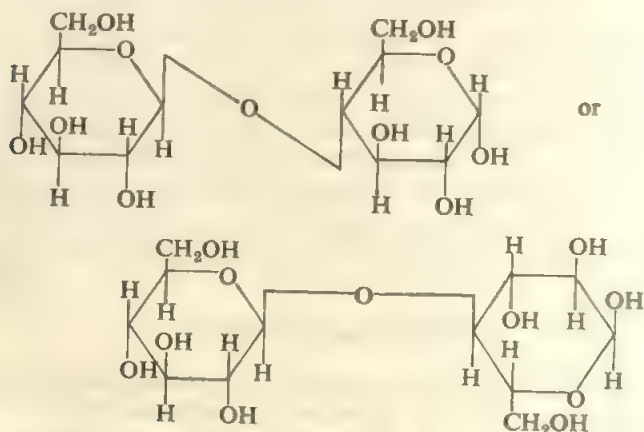


The presence of a free hydroxyl group attached to carbon 1 on the unit on the right makes this a potential aldehyde group. Maltose is therefore a reducing sugar which would be expected to show mutarotation and to react with Tollens', Fehling's and Benedict's reagents, which it does. Like glucose, it forms a phenylosazone of characteristic crystalline appearance.

Maltose is used in baby foods and malted milk. It is particularly important as an intermediate in the manufacture of ethyl alcohol from starch. The first step in the digestion of starch is its hydrolysis to maltose. The enzyme maltase in the small intestine completes its conversion into glucose.

### B. CELLOBIOSE

Cellobiose is a beta glucoside. The R— group is a second molecule of glucose. It consists of two glucose units joined by a beta glucosidic linkage from carbon 1 of one unit to carbon 4 of the second. Its formula is

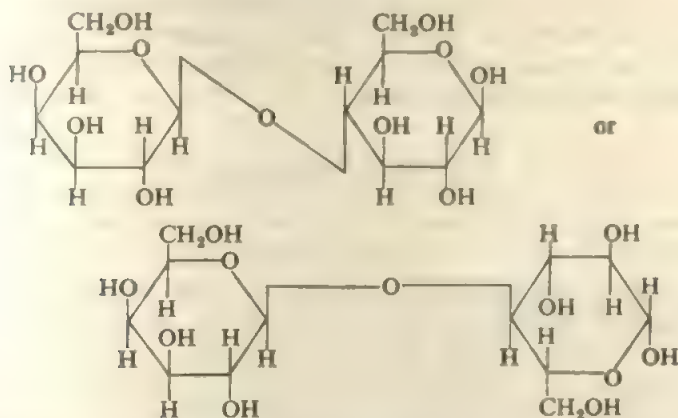


Since cellobiose has a free hydroxyl attached to carbon 1 of the unit to the right, it is a reducing sugar and shows the corresponding reactions. It is obtained by careful hydrolysis of cellulose. The distinctive difference between cellobiose and maltose, the type of glucosidic linkage present, is important in determining the structure and nature of the polysaccharides formed from glucose. The cellobiose formula (lower) was obtained by rotating the glucose unit on the right through an angle of  $180^\circ$ , to give a better picture of the actual molecule.

### C. LACTOSE

Lactose, a reducing sugar, is the important carbohydrate in milk. It is commonly referred to as milk sugar. Human milk contains 5 to 8 per cent and cow's milk 4 to 6 per cent. Hydrolysis of lactose yields both glucose and galactose. In contrast to maltose and cellobiose, lactose is a beta galactoside, in which the two component monosaccharides are joined through a galactosidic

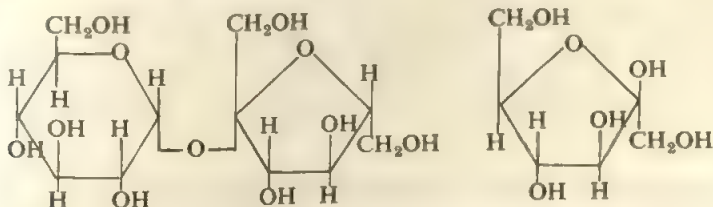
linkage between carbon 1 of the galactose and carbon 4 of the glucose unit. Its formula is:



Lactose forms an osazone having characteristic crystals which are of great value in indicating the presence of this sugar. It is readily fermented to lactic and butyric acids. This is of use in the making of cheese.

#### D. SUCROSE

Sucrose (table sugar) is produced in larger quantities today than any other organic chemical manufactured as a pure compound. It is obtained commercially from sugar cane and sugar beets. Although its structure has been known for many years, its chemical synthesis was not accomplished until very recent times (1957), and then in milligram quantities. Sucrose is used principally as a food. Hydrolysis of sucrose yields glucose and fructose in equal molar quantities, a mixture often referred to as invert sugar. Structurally, sucrose is both a fructoside and a glucoside, since the two monosaccharide units are joined from carbon 2 of the fructose to carbon 1 of the glucose unit. The fructose component of this disaccharide is beta fructose, and the glucose component is alpha glucose. The structure of sucrose may be written:



Note that to place the beta hydroxyl on carbon 1 of the fructose next to the alpha hydroxyl attached to carbon 1 of glucose, it is necessary to rotate the fructose through  $180^\circ$ , a transformation which puts all the groups which are *up* in the formula on the right, *down* in the structure written for sucrose.

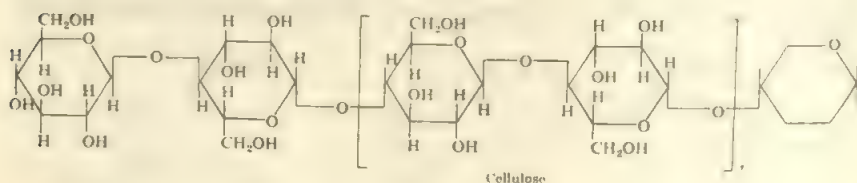
Hydrolysis of sucrose is often referred to as an inversion. The specific rotation of pure sucrose is  $-66^\circ$ . The specific rotation of the equal molar mixture of fructose and glucose is  $+20^\circ$ . This conversion of a dextro (+) rotation solution into one having a levo (-) rotation is called inversion. The  $+20^\circ$  is an average of the  $+52^\circ$  due to the glucose and the  $-90^\circ$  due to the fructose dissolved in the solution.

#### 4. POLYSACCHARIDES

Polysaccharides are polymers in which one finds the component monosaccharide units joined to each other by glycosidic linkages. Polysaccharides found in nature are molecules of high molecular weight, and correspondingly consist of large numbers of monosaccharide units. In many of these, D-glucose is the sole, or major, component. However, polysaccharides containing D-mannose, D- and L-galactose, D-xylose and L-arabinose are known. Likewise, polysaccharides formed from sugar derivatives such as glucuronic acid or glucosamine have been found. Chitin, mentioned earlier, is a polymer of acetylated glucosamine. Polysaccharides differ structurally as well as in their monosaccharide components. The most important polysaccharides are starch, glycogen and cellulose. Others of interest include inulin, gums and pectins.

##### A. CELLULOSE

Cellulose is the polysaccharide discussed first because it is the most abundant of the polysaccharides, comprising 50 per cent or more of all the carbon in vegetation. The source of the purest cellulose is cotton. Complete hydrolysis of cellulose yields only D-glucose and, as pointed out in an earlier section, its careful partial hydrolysis yields cellobiose. The formation of cellobiose shows that the glucose units in cellulose are united through beta linkages. Cellulose is therefore a linear polymer of a large number of  $\beta$ -D-glucose units joined from carbon 1 of one unit to carbon 4 of the next unit. The structure may be written in the following way:



The molecular weights of celluloses obtained from different sources and by various methods have been estimated to be between 50,000 and 500,000.

The average number of glucose units in the different samples of cellulose, therefore, range between about 300 and 2500 units per molecule. In the structure given above,  $n$  will be equal to some number between 150 and 1250. Celluloses with the lower molecular weights are probably degradation



products of the larger polymers. It is unlikely, however, that all molecules of native cellulose are of the same weight.

Cellulose is insoluble in water and in all organic solvents. It does not react with Tollens', Fehling's and Benedict's reagents, nor does it form a phenylhydrazone. It dissolves in a variety of special reagents, such as an ammoniacal solution of cupric sulfate (Schweitzer's reagent), from which cellulose may be precipitated to produce rayon fiber. Many types of rayon and other derivatives have been prepared by chemical modification of cellulose.

### B. STARCH

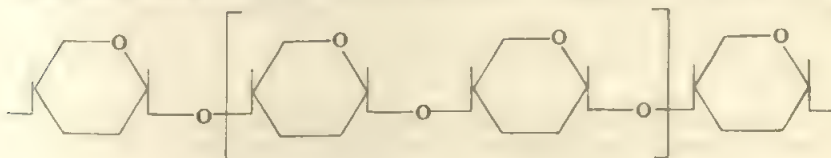
The polysaccharide starch serves as the nutritional reserve carbohydrate in many plants. It is chiefly concentrated in the seeds and roots. On complete hydrolysis, starch yields glucose as the only monosaccharide. Enzymatic hydrolysis gives relatively large amounts of maltose, which indicates that the glucose units in starch are joined through alpha-glucosidic linkages. Starch is clearly a polymer of  $\alpha$ -D-glucose.

Starch in its native state is observed as microscopically visible granules. The starch grains of plants differ in size and shape; these differences are apparent when seen under the microscope and their appearance may be used to identify the source.

Starches found in nature contain in general two types of compounds, amylose and amylopectin, which are separable from each other. On heating starch with water, a soluble portion (amylose) is obtained, and an insoluble pastry material (amylopectin) remains. Since both of these substances are composed of  $\alpha$ -D-glucose, they must differ structurally.

### C. AMYLOSE

The polysaccharide amylose is believed to be composed of long, unbranched chains of glucose units. As a linear polymer it resembles cellulose; however, it has a lower average molecular weight, which ranges between 10,000 and 50,000. This indicates that there are 60 to 300 units in each molecule of this component of starch. The structure of amylose may be written as follows:



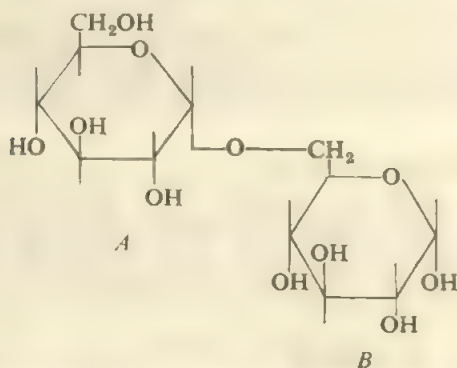
Maltose unit

Here the repeating unit is maltose, in contrast to the repeating cellobiose units in cellulose. Amyloses give a deep-blue color with iodine (in contrast to the red-purple color formed with amylopectins). Potato starch contains about 20 per cent of the amylose fraction, a proportion found also in many other starches. The remainder is amylopectin. The exact per cent of each varies from starch to starch.

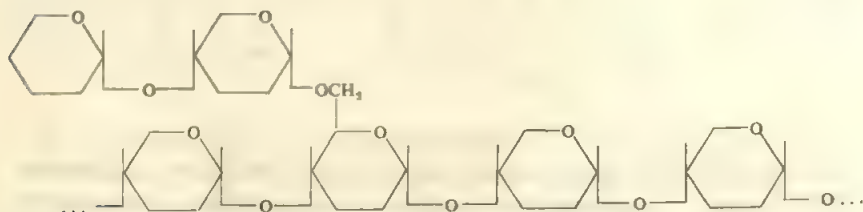
## D. AMYLOPECTIN

Amylopectins are composed of molecules larger than those of the amyloses. They differ from amylose in having a branched-chain structure. Amylopectins have one chain-terminal glucose for every 24 to 30 glucose units in the molecule. Molecular weights up to 300,000 or more have been found. This corresponds to molecules having around 1800 glucose residues per molecule. With branching occurring often enough so that each branch has only 24 to 30 units, a molecular weight of 300,000 would correspond to a molecule with over 60 branching points.

Branching results from the linking of glucose units to a polymeric chain through one or more of the hydroxyl groups not utilized in forming the linear structure. Branches appear to be the result of the joining of certain glucose units through carbon 1 of the first unit to carbon 6 of the second unit. A disaccharide of the formula below illustrates this:



This disaccharide is known as *melibiose*. Two glucose molecules may be joined in this way, even if the glucose unit *B* is already attached to neighboring glucose units through alpha glucosidic linkages between carbons 1 and 4. Whenever a glycosidic linkage from carbon 1 to carbon 6 occurs along a glucose chain, a branch appears. The following formula shows this:



In simpler language, amylopectin is a treelike molecule in contrast to the linear arrangement in amylose. This highly ramified structure permits the formation and existence of the bigger insoluble molecules.

## E. GLYCOGEN

In the animal body the polysaccharide glucose is stored in both the liver and the muscles as glycogen. Structurally, glycogen is a branched-chain polysaccharide, resembling amylopectin. Glycogen consists largely of  $\alpha$ -D-glucose units 1,4-linked through glucosidic bonds with considerable branching involving 1,6-linkages. Glycogen differs from amylopectin in being more highly branched, having one chain-terminal glucose for every 12 to 20 glucose units. Glycogens have molecular weights ranging from about 250,000 to several millions, which require the presence of 1500 to 20,000 residues per molecule. Molecular sizes vary widely even within samples obtained from a single source.

Glycogen occurs in animal cells in smaller particles than are normally observed for starch granules. It gives a violet-red color with iodine and is quite stable with alkali, but it undergoes acid hydrolysis quite readily. It is precipitated from solution with alcohol.

## EXERCISES

- Define:
 

<ol style="list-style-type: none"> <li>a. carbohydrate</li> <li>b. aldohexose</li> <li>c. ketohexose</li> <li>d. monosaccharide</li> <li>e. oligosaccharide</li> <li>f. polysaccharide</li> <li>g. mutarotation</li> <li>h. hemiacetal</li> </ol>	<ol style="list-style-type: none"> <li>i. alpha sugar</li> <li>j. dextrose</li> <li>k. epimers</li> <li>l. glycoside</li> <li>m. <math>\sigma</math>-glucoside</li> <li>n. an invert sugar</li> <li>o. blood sugar</li> </ol>
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- Name four hexoses that occur in nature either as monosaccharides or as units in other molecules.
- Why are there no ketobioses?
- Why is glucose considered the most important hexose?
- Explain the significance of each fragment of the name D-(+)-glucose.
- Give some experimental evidence for each of the following facts: Glucose
  - a. has the formula  $(\text{CH}_2\text{O})_6$
  - b. is a straight chain compound
  - c. is an aldehyde
  - d. has 5 hydroxyl groups
- Use structural formulas to explain the mutarotation of D-glucose.
- Write open chain formulas for
  - a. D-glucose
  - b. D-mannose
  - c. D-fructose
  - d. D-galactose
- Explain the structural differences between cellobiose, sucrose, maltose and lactose.
- Explain the structural similarities and differences between (a) starch and cellulose, (b) amylose and amylopectin, (c) amylopectin and glycogen.
- What color is formed with iodine and each of these: (a) starch, (b) amylose, (c) amylopectin, (d) glycogen?
- Compare the relative molecular weights of (a) glucose, (b) sucrose, (c) cellobiose, (d) dextrans, (e) amylose, (f) amylopectin, (g) cellulose, (h) starch, (i) glycogen.
- What structural characteristics are necessary if a disaccharide is to be a reducing sugar?
- What is Tollens' reagent, Benedict's solution, and Fehling's solution?
- What kind of a product is formed when an aldohexose is oxidized mildly? When it is oxidized with hot nitric acid?
- Compare the polymers: (a) starch, (b) cellulose, (c) silk, (d) polyethylene.

BIOCHEMISTRY, AN  
INTRODUCTION

When the study of the chemistry of the compounds of carbon (Chapter 29) was initiated, the point was made that the title "Organic Chemistry" came into wide use because organic compounds were first obtained only from plants and animals. They appeared to have a unique association with life. Organic chemistry has no such limitations today. Many organic compounds do, however, have important functions in and are obtainable only from living plants, animals or microorganisms. Proteins, carbohydrates and fats are examples of such substances. Proteins, in particular, have an association with life processes so clear and unique that many consider the ability to synthesize protein, essentially a chemical process, to be the one property most characteristic of living organisms and of life itself. Irrespective of how one may define life, from the chemical standpoint, muscle contraction, vision, absorption of foods and nerve conduction as vital processes are maintained only through a complex set of chemical and physical changes so adjusted as to provide both the energy and the chemical compounds required.

Because of the close tie between chemistry and biological processes, a field of study referred to as biochemistry has evolved and grown into a major discipline. Knowledge of the subject matter of this field contributes greatly to the understanding of many principles of zoology, botany and the other fields of biology. Modern courses in biology lean heavily on chemistry in explaining essential biological phenomena.

Biochemistry seeks to discover, describe and explain the variety of chemical and physical processes which take place in living organisms. For the chemist it is the field which focuses on the chemical events which maintain life. Others consider it to be one of the life sciences, a point of view based on the fact that the subject of its study is the living organism. In essence, the biochemist uses chemical methods to study biological phenomena and from his



observations seeks to understand cellular changes through use of recognized chemical and physical laws. One important objective of biochemistry is to bridge the gap, large as it is, which exists between the highly integrated activity of the living cell and the properties of the individual components which go to make up the cell. The study of biochemistry will be introduced in this chapter by an examination of several important chemical reactions and processes which occur within cells. Several essentially biological phenomena will be described and some significant factors in achieving biological reactions will be discussed. Earlier consideration of this topic has been delayed because a basic knowledge of chemistry and particularly of organic reactions is fundamental for understanding the various events which characterize biological processes.

Wherever one examines the world of living things in detail, chemical changes are found to be taking place. Within all living organisms foodstuffs undergo profound chemical changes. The totality of these chemical transformations which substances experience is called metabolism. Included are all changes which a nutrient undergoes from the moment of its entry into the organism until that moment when a product formed is used for the synthesis of other compounds or is discharged as waste. Based on the observation that a variety of intermediate products ("intermediates") are formed during the conversion of most nutrients into ultimate products, metabolism is frequently referred to as "intermediary metabolism." Two other terms, anabolism and catabolism, descriptive of different aspects of metabolism, are also used. For example, green plants use solar energy to make a variety of complex organic compounds from simple starting materials such as water, carbon dioxide and small amounts of other inorganic compounds such as nitrates and phosphates. This formation of larger, sometimes rather complex molecules, from simple starting materials in living organisms is called *anabolism*. Such reactions or processes require energy. Living organisms also have the ability to decompose or degrade larger molecules into smaller ones. Reactions or processes of this kind provide a net yield of energy and constitute the phase of metabolism called *catabolism*. Catabolism permits cells to exploit, for their own use, the chemical energy which is locked up within the different compounds which reach them. In this way cells obtain all the energy which must be expended to accomplish their various anabolic reactions and for carrying on bodily functions.

Metabolism serves as an example of an essentially biological phenomenon. It accomplishes two things; (1) it provides the energy required of all organisms for maintaining life, and (2) it achieves the conversion of dietary constituents into cellular components. Catabolism and anabolism, two opposing aspects of metabolism, constitute a dynamic system in which both are taking place simultaneously and continuously. When a proper balance exists between them, the organism experiences normal growth, development and function.

Chemically, metabolism consists of a sequence of related interconnected chemical reactions. The sequence of equations outlining in order the series

of reactions by which a particular substance is transformed within a cell is referred to as a *metabolic pathway*. One such sequence is the Embden-Meyerhof pathway\* for the conversion of glucose or glycogen into pyruvic acid, which is outlined in Figure 40.1. This series of reactions provides a limited amount of energy for cellular processes; but, more importantly, it accomplishes the conversion of a 6-carbon sugar into two molecules of a three carbon compound which can be readily oxidized to provide additional energy—and, as a matter of fact, to provide the bulk of the energy which is recovered by the cell from the degradation of glucose. Each reaction shows only the important metabolic change which occurs and does not include all the reactants required. For example, a phosphorus compound is required to provide the phosphate for the formation of glucose-6-phosphate from glucose.

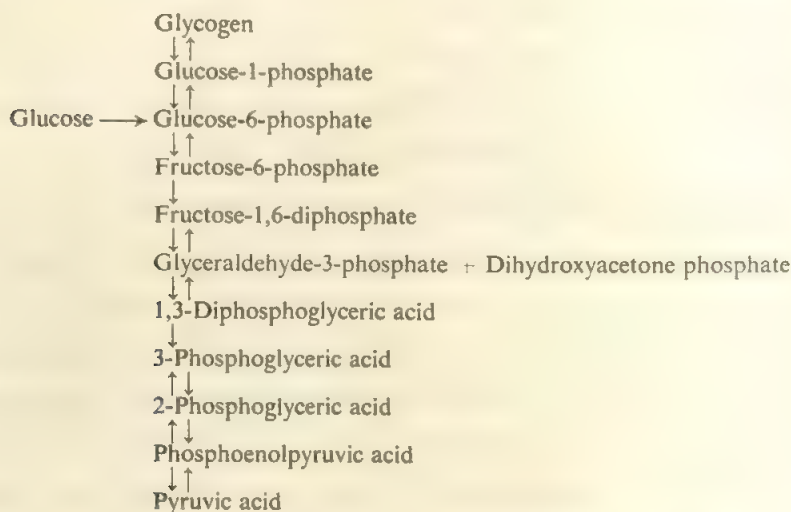
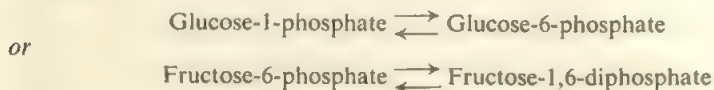


Figure 40.1. Embden-Meyerhof pathway for metabolism of glucose.

Each reaction of the pathway is referred to as a metabolic or biochemical reaction. Both terms will be used when referring to individual reactions. Any one of the transformations shown in Figure 40.1 serves as an example of such a reaction; for example,



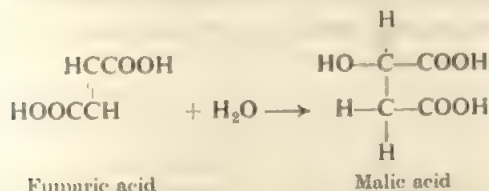
Biochemical reaction is thus a descriptive term used to designate a certain chemical transformation which a substance experiences in a living cell.

As is the case with all chemical reactions, biochemical transformations are

\* Named after G. Embden and O. Meyerhof, whose studies led to the discovery of this pathway.

controlled by the concentrations of reacting substances and the energy changes involved. However, they are, in addition, subject to other controlling factors and influences to which most organic reactions performed outside cells are not. Included is physiological control by the nervous system and by hormones produced in the glands of internal secretion (endocrine glands) such as the pituitary, adrenal or thyroid.

If metabolic reactions are compared in other ways with nonbiologically controlled organic reactions, one is immediately struck by the speeds with which they proceed in cells under the mild conditions of temperature and pH of the physiological environment, and by the highly specific nature (specificity) of the changes which take place. For example, an important intracellular ("in vivo") reaction, hydration of fumaric acid, may be compared with its chemical hydration outside the cell ("in vitro").



Under physiological conditions (Temperature = 37°C; pH 7.34) this reaction takes place rapidly and smoothly while producing only one product, D-(—)-malic acid. In contrast, chemical hydration with water outside the cell occurs only under much more drastic conditions (Temperature = 150–160°C in a closed tube), and then not too readily, to produce a non-specific racemic mixture of both optical isomers of malic acid. One is equally impressed with the sequential and predominantly cyclic pattern found for many of the processes used to achieve rather complex transformations.

As indicated, the rates of many chemical reactions within cells is impressive. It becomes more so when, as illustrated above, it is found that many of these same reactions when attempted outside the cell under much more drastic conditions proceed too slowly to be measurable or even, in some cases, to be detectable. Why this is found to be true and how such rapid rates are achieved inside cells have always been of great scientific interest.

The rapid rates of metabolic reactions have been shown to be due to the presence in cells of special catalysts called *enzymes*. Catalysts, as you may recall, are substances which speed up the rates of chemical reactions when present in extremely small amounts without undergoing any permanent change or being consumed in the process. Enzymes, in addition to catalyzing reactions, also determine the type of reaction and, thus, the nature of the product which will be obtained from a given reactant. This may be referred to as their *directive effect*. Enzymes, because of these capabilities, that of catalyzing reactions and of determining the direction in which the reaction will proceed are of great importance and will be considered in more detail.

Chemically, enzymes are proteins (see Chapter 38) and are, themselves, products of cellular metabolism. Being proteins they are chemical compounds

susceptible to the same chemical reactions and modifications as all other proteins. For example, most enzymes are unstable to heat, a characteristic of most proteins. Enzymes, when kept at too elevated a temperature for very long, undergo structural changes (denaturation) which often include the loss of the ability to function.

The most characteristic property and function of an enzyme is the ability to catalyze chemical reactions. Catalysis is accomplished through a set of reactions (see Fig. 40.2) which includes, first, a rapid reaction between the enzyme present and a reactant referred to as the substrate. As a result of the rapid reaction between the enzyme and substrate, an enzyme-substrate compound (or complex) is formed. This compound then undergoes, in a second step, a somewhat slower reaction in which it decomposes or separates into products and enzyme. The enzyme is recovered unchanged and becomes available for recombination with another molecule of substrate. This then permits the entire process to repeat itself with more substrate. Such repetition may continue over and over again.

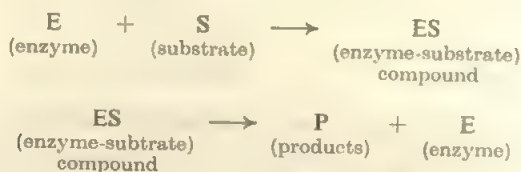


Figure 40.2. Mechanism of enzyme catalysis.

This picture for the catalytic function of an enzyme is referred to as the Michaelis-Menten hypothesis.\* The idea rests on a firm experimental foundation, although the nature of the ES compound has been directly demonstrated for only a few enzymes. The lifetime of the complex is extremely short, making detection of the complex difficult because of rapid decomposition into products. According to this concept of enzyme function, it is apparent that one enzyme molecule could achieve conversion of many molecules of substrate into products. It, therefore, serves to explain why only small amounts of enzyme are required. As will be discussed, the combination of enzyme and substrate also aids in explaining the specificity of enzymes.

It should be emphasized at this stage that an enzyme contributes no energy to the overall reaction. Thus each reaction which is catalyzed must be an energetically possible reaction without the enzyme being present. Enzymes merely increase the rate of formation of products. The final yield of product in the presence of the enzyme is the same as that gained without the enzyme. Reaction in the absence of the enzyme takes much longer and sometimes, as indicated earlier, is so slow as to be almost undetectable during a reasonable

\* Named after the investigators, L. Michaelis and M. L. Menten, who offered the first mathematical treatment of this concept.



time of observation. Table 40.1 gives some relative rates for the decomposition of  $\text{H}_2\text{O}_2$  into water and oxygen,  $2 \text{H}_2\text{O}_2 \rightarrow 2 \text{H}_2\text{O} + \text{O}_2$ , when conducted under the same conditions with and without catalysts present.

Note that the enzyme catalyzed decomposition of  $\text{H}_2\text{O}_2$  proceeds about ten times faster than the reaction without a catalyst and two to three times as fast as its decomposition in the presence of the inorganic catalysts,  $\text{MnO}_2$  or Pt. Sucrose hydrolyzes about 14 times as rapidly in the presence of invertase as in acid solution.

From the discussion it is evident that combination of the enzyme with its substrate and the structural adjustments which such a combination requires achieves the more rapid rates of formation of product. It is perhaps better to say, however, that the rate increase results from the readjustment in bond energies within the substrate necessary to accommodate the union with the enzyme. The real question as to what happens when the enzyme-substrate complex is formed to make the increased rate possible, however, remains unanswered and unresolved. Possible explanations of the phenomenon can be reached through application of concepts of physical chemistry concerning the action of catalysts in general, but these still leave the detailed mechanism in doubt.

As stated, metabolic reactions are highly specific with regard to both the type of substrate involved and the particular reaction which the substrate undergoes. Each reaction proceeds in a manner such as to produce a specific change in the compound concerned. For example, glucose-6-phosphate is capable of being transformed directly into several different products, namely, glucose-1-phosphate, fructose-6-phosphate, glucose or 6-phosphogluconolactone.

**Table 40.1. Rates of Enzyme Catalyzed Reactions**

Reaction	Catalyst	Relative Ratio	
		Rates ( $0^\circ\text{C}$ )*	Rate Enzyme Reaction
			Rate Nonenzyme Reaction
Decomposition of $\text{H}_2\text{O}_2$	None	3.75	—
	$\text{MnO}_2$	8.50	4.3
	Colloidal Pt	11.90	3.1
	Liver catalase	36.7	9.8
Hydrolysis (inversion) of sucrose	$\text{H}_3\text{O}^+$ (acid)	0.87	—
	Yeast invertase	12.3	14.1

\* Compared to rate of reaction at  $30^\circ\text{C}$  set equal to 100.

- (1) Glucose-6-phosphate  $\longrightarrow$  Glucose-1-phosphate
- (2) Glucose-6-phosphate  $\longrightarrow$  Fructose-6-phosphate
- (3) Glucose-6-phosphate +  $\text{H}_2\text{O}$   $\longrightarrow$  Glucose +  $\text{H}_3\text{PO}_4$
- (4) Glucose-6-phosphate  $\longrightarrow$  6-Phosphogluconolactone +  $2\text{H}$

Each reaction yields a different product. The product formed within the cell is determined by the type of enzyme present at the site of reaction. Each enzyme has the capability of selecting and catalyzing one from among all the possible reactions. Glucose-6-phosphate is converted into glucose-1-phosphate if the enzyme phosphoglucomutase is present. With phosphoglucosomerase, reaction (2) takes place to give fructose-6-phosphate. Should the enzyme, phosphatase, be present, glucose-6-phosphate is hydrolyzed to glucose and phosphoric acid as shown in reaction (3). 6-Phosphogluconolactone is formed when glucose-6-phosphate is oxidized under the influence of the enzyme glucose-6-phosphate dehydrogenase as shown in reaction (4). Only if all four enzymes mentioned above are present can all four products be expected.

Each enzyme, thus, carries an inherent or built-in capability for catalyzing a particular reaction with certain substrates. This capability is referred to as its *specificity*. Enzymes are highly specific catalysts. Catalysis, as shown above, is dependent upon and arises from combination of an enzyme with a substrate. Specificity, likewise, may be pictured as being an expression of this combination. Specificity, thus, becomes not some mysterious property of an enzyme, but a phenomenon resulting from a structural kinship between substrate and enzyme. Specificity is a reflection of both (1) the way in which the enzyme unites with the substrate, and (2) how well this attachment of substrate to enzyme takes place. For example, since four different products are obtainable from glucose-6-phosphate, depending upon which of four different enzymes are present, it may be assumed that each enzyme unites with glucose-6-phosphate in a different way. The type of combination which occurs predetermines the reaction which will take place and the products which will form. The rate of appearance of product however will be dependent upon how well the combination takes place. Specificity reflects an overall relationship between the structural features of the enzyme and substrate. The relationship either facilitates or hinders satisfactory combination. If a close reciprocal structural relationship or fit between enzyme and substrate exists, they combine firmly in such a way that a particular reaction occurs. Without a fit the enzyme-substrate complex does not form and no reaction takes place. A partial combination with a structurally similar compound may occur, in which case reaction sometimes takes place but usually at a greatly reduced rate. Also, combination of the enzyme with a foreign unreactive substance can prevent reaction by excluding unreactive substrate from the enzyme surface or active site. Substances which combine with the enzyme and prevent it from functioning as a catalyst are called *inhibitors*.

The lock and key relationship serves to illustrate this idea or concept of structural fit. Only those keys (substrates) which fit properly into the lock ("active site of the enzyme") induce the lock (enzyme) to open up (catalyze the reaction). The general idea is illustrated in Figure 40.3.

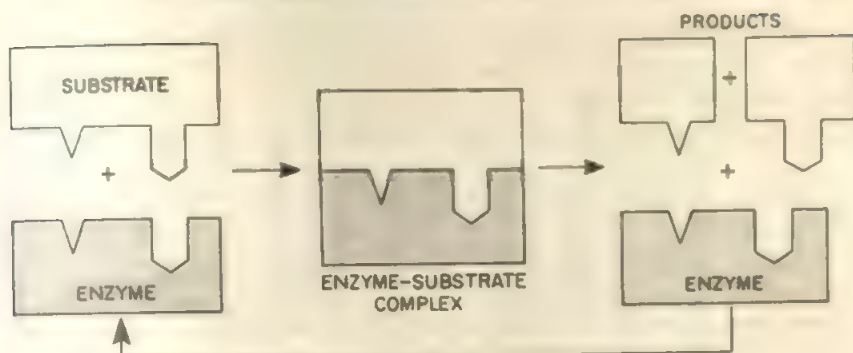


Figure 40.3. Enzyme-substrate combination.

Although our present view concerning how enzymes function, when examined in detail, is much more sophisticated than the lock and key analogy, the idea serves reasonably well as an illustration for the concept that specificity depends on and is determined by the degree of structural matching between enzyme and substrate. Matching permits only certain reactions to occur (at reasonable rates) and particular products to form. The enzyme present, because of the structural features it demands in any substrate with which it combines, directs the course of the reaction and determines the products formed.

In summary it can be stated that the concept which assumes a combination between enzyme and substrate can account quite satisfactorily for the two most characteristic features of enzyme function—their ability to catalyze reactions and their high specificity with regard to types of reactions catalyzed and substrates transformed.

Let us now return to a consideration of the sequential and cyclic nature of metabolic processes. Each reaction of a metabolic pathway is catalyzed by a specific enzyme. A different enzyme is required for each reaction. Any pathway, therefore, becomes a multienzyme system composed of a sequence of enzyme-catalyzed reactions which require careful control and coordination. This illuminates the necessity for the variety of controls, neural, hormonal and enzymatic, which influence cellular processes. The pattern of reactions of one pathway, the Embden-Meyerhof scheme shown in Figure 40.1, has already been outlined. Let us now examine this pathway in more detail.

The formation of pyruvic acid from glucose involves a series of ten reactions, each of which accomplishes only a small, though important, change in the structure of the product of the preceding reaction. As an initial stage, either glucose or glycogen, depending upon the cell which is studied, is converted into a phosphomonoester of glucose. This appears to be necessary because the enzymes concerned with glucose metabolism by this pathway act only on phosphorylated derivatives. Note that each of the intermediates in the sequence of reactions is a phosphate derivative. Not included as intermediates are glucose or glycogen and the final product pyruvic acid. Combination with phosphate seems to activate the bond of the derivatives, so the reactions outlined take place readily.

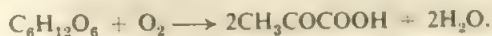
**Table 40.2. Reaction and Enzymes of the Embden-Meyerhof Pathway of Glucose Metabolism**

<i>Reaction</i>	<i>Enzyme</i>	<i>Type of change</i>
Glycogen → Glucose-1-phosphate	Phosphorylase	Phosphorylation
Glucose-1-phosphate → Glucose-6-phosphate	Phosphoglucomutase	Phosphate interchange
Glucose → Glucose-6-phosphate	Hexokinase	Phosphorylation
Glucose-6-phosphate → Fructose-6-phosphate	Phosphoglucose isomerase	Isomerization
Fructose-6-phosphate → Fructose-1,6-diphosphate	Phosphofructokinase	Phosphorylation
Fructose-1,6-diphosphate → Glyceraldehyde-3-phosphate	Aldolase	Cleavage of C—C bond
+		
Dihydroxyacetone phosphate		
Dihydroxyacetone phosphate → Glyceraldehyde-3-phosphate	Triosephosphate isomerase	Isomerization
Glyceraldehyde-3-phosphate → 1,3-diphosphoglyceric acid	Phosphoglyceraldehyde dehydrogenase	Oxidation and Phosphorylation
1,3-diphosphoglyceric acid → 3-Phosphoglyceric acid	Phosphoglycerate kinase	Loss of phosphate
3-Phosphoglyceric acid → 2-Phosphoglyceric acid	Phosphoglyceromutase	Phosphate interchange
2-Phosphoglyceric acid → Phosphoenolpyruvic acid	Enolase	Loss of water
Phosphoenolpyruvic acid → Pyruvic acid	Pyruvic kinase	Transfer of phosphate



Each reaction, the name of the enzyme which catalyzes the reaction and the type of change which is achieved by the reaction are summarized in Table 40.2. Only one step in this sequence involves an oxidation. Both oxidation and phosphorylation are required for the conversion of 3-phosphoglycer-aldehyde into 1,3-diphosphoglyceric acid.

The net result of the sequence of reactions from glucose to pyruvic acid is the oxidation of glucose accompanied by cleavage into two molecules of pyruvic acid,



Note that for each glucose (or glucose-6-phosphate) molecule transformed by way of this pathway two molecules of pyruvic acid are obtained. This follows from the fact that the dihydroxy acetone phosphate is directly converted into 3-phosphoglycer-aldehyde and is thus ultimately transformed into pyruvic acid.

Pyruvic acid, however, does not usually accumulate in cells because of further reaction. The further reaction which it experiences depends upon the type of cell in which it is metabolized. Glucose, when fermented (yeast cells), is initially converted into pyruvic acid through the sequence of reactions outlined in Figure 40.1. However, to complete the fermentation process which yields alcohol, pyruvic acid undergoes a loss of carbon dioxide and reduction to give ethanol. On the other hand, in muscle cells, the pyruvic acid, rather than giving alcohol, is reduced directly to lactic acid without loss of carbon dioxide. In muscle the source of glucose is glycogen stored in muscle cells, and the sequence of reactions by which lactic acid is formed from glycogen is referred to as glycolysis. The reactions which produce pyruvic acid from glucose-6-phosphate in both fermentation and glycolysis are the same. Fermentation and glycolysis differ only in the source of the glucose-6-phosphate utilized and in the disposition of the pyruvic acid formed. In fermentation glucose-6-phosphate is obtained by direct phosphorylation of glucose, whereas in muscle cells it arises from glucose-1-phosphate which is formed directly from muscle glycogen. Fermentation and glycolysis can both be accomplished anaerobically—without oxygen—providing the oxidation of 3-phosphoglycer-aldehyde to 1,3-diphosphoglyceric acid is coupled with the reduction of pyruvic acid to ethanol or lactic acid.

The degradation of glucose, however, is more often carried out with oxygen readily available within the yeast or muscle cell. Normally, pyruvic acid is oxidized to carbon dioxide and water without formation of either alcohol or lactic acid. Lactic acid accumulates in muscle only when the supply of oxygen is not sufficient to permit oxidation of all the pyruvic acid formed. Oxidation of pyruvic acid is accomplished through a combination of metabolic reactions (a cycle of reactions) referred to as the TCA\* or citric acid cycle. The citric acid cycle is one of the most important metabolic pathways found in cells and is presented here (see Fig. 40.4) to illustrate the cyclic nature of many biological processes. The sequence of reactions may be pictured as starting and terminating with the same compound, *oxaloacetic acid*.

\*TCA = Tricarboxylic acid cycle.

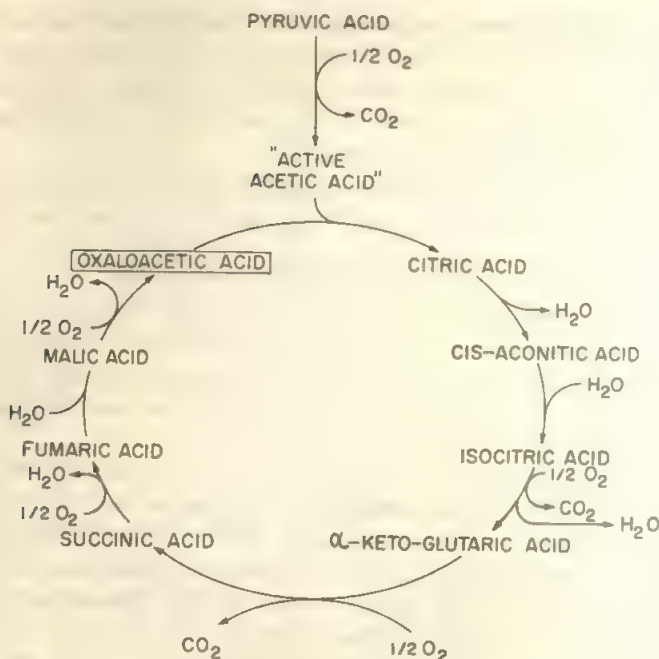
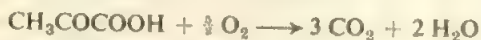


Figure 40.4. Citric acid cycle.

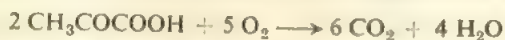
Pyruvic acid enters the reaction cycle following its conversion into "active" acetic acid\* through a reaction in which pyruvic acid undergoes oxidation and loss of carbon dioxide.



The "active" acetic acid enters the cycle by reacting with oxaloacetic acid to form citric acid, which then experiences the sequence of reactions outlined in Figure 40.4, the end-result of which is the reformation of a molecule of oxaloacetic acid. The regenerated oxaloacetic acid can again react with "active" acetic acid and repeat the cycle. One trip through the cycle of reactions, oxaloacetic acid to oxaloacetic acid, accomplishes the conversion of one "active" acetic acid into carbon dioxide and water. The net result starting with pyruvic acid is the transformation of one molecule of pyruvic acid into  $\text{CO}_2$  and water,



The oxidation of the two molecules of pyruvic acid obtained from glucose in fermentation or glycolysis requires that two molecules traverse the cycle. The equation for the oxidation of two molecules is as shown below:

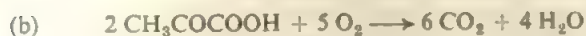


\* "Active" acetic acid is known to be acetyl coenzyme A. Details of its composition and structure can be obtained by consulting a standard textbook of biochemistry.

In summary, if one molecule of glucose is subjected to the Embden-Meyerhof pathway and the Citric Acid Cycle in turn, the chemical change accomplished is the complete degradation of glucose to carbon dioxide and water. The Embden-Meyerhof phase achieves the conversion of one glucose into two molecules of pyruvic acid,



which are then completely oxidized to  $CO_2$  and water through the Citric Acid Cycle,



The sum of equations (a) and (b) gives the net equation for the oxidation of glucose to carbon dioxide and water by these pathways,



The equation shows only the overall transformation which has occurred. The manner in which it is accomplished in the cell comes only from a knowledge of the metabolic pathways utilized by the various organisms which utilize glucose.

The Embden-Meyerhof pathway and the Citric Acid Cycle have been offered as illustrations of typical metabolic pathways. Actually, they are the pathways used by many organisms to accomplish the oxidation of glucose. Other pathways, however, are known for glucose oxidation. Related pathways are known for amino acids and lipids. The schemes outlined illustrate how individual biochemical reactions may be linked together in a sequence to achieve particular biological transformations. Of particular interest and importance are the cyclic processes illustrated by the Citric Acid Cycle. Cycles of reactions are essential because they provide the only means by which a starting point can be restored if any one of the reactions of a sequence is irreversible. Metabolic cycles provide for economy in use of materials, because compounds essential to functioning of a pathway can be used and regenerated over and over again. A cyclic pathway such as the Citric Acid Cycle is essentially a metabolic machine set up to accomplish a particular type of chemical change. In the case of the Citric Acid Cycle, one of its primary functions is the conversion (oxidation) of "active" acetic acid into carbon dioxide and water with energy being released for use or storage. Many other cyclic processes have been discovered which serve as vital metabolic pathways of living organisms.

## QUESTIONS

1. What is an important goal of biochemistry?
2. Give three examples of a metabolic reaction.
3. What is an intermediate when used in connection with metabolism?
4. What is the difference between anabolism and catabolism?
5. Why is metabolism a useful process for living cells?
6. What is an enzyme?

7. What is a biochemical reaction?
8. Why does a reaction within a cell often go much faster than the same reaction performed outside the cell?
9. What determines the type of product formed from glucose-6-phosphate within a cell?
10. What is specificity? How may this be achieved by an enzyme?
11. Outline the TCA cycle. What is an important function of this cycle?
12. Which reaction of the Embden-Meyerhof pathway includes an oxidation?
13. Outline the sequence of reactions commonly referred to as fermentation of glucose.
14. What is an inhibitor?
15. How much faster does the inversion of sucrose take place when invertase is present than inversion in the presence of  $H^+$ ?
16. What is the Michaelis-Menten mechanism for enzyme catalysis?
17. Name the enzymes which catalyze the reactions: glucose-1-phosphate to glucose-6-phosphate, fructose-6-phosphate to glucose-6-phosphate, 3-phosphoglyceric acid to 2-phosphoglyceric acid, phosphoenolpyruvic acid to pyruvic acid.



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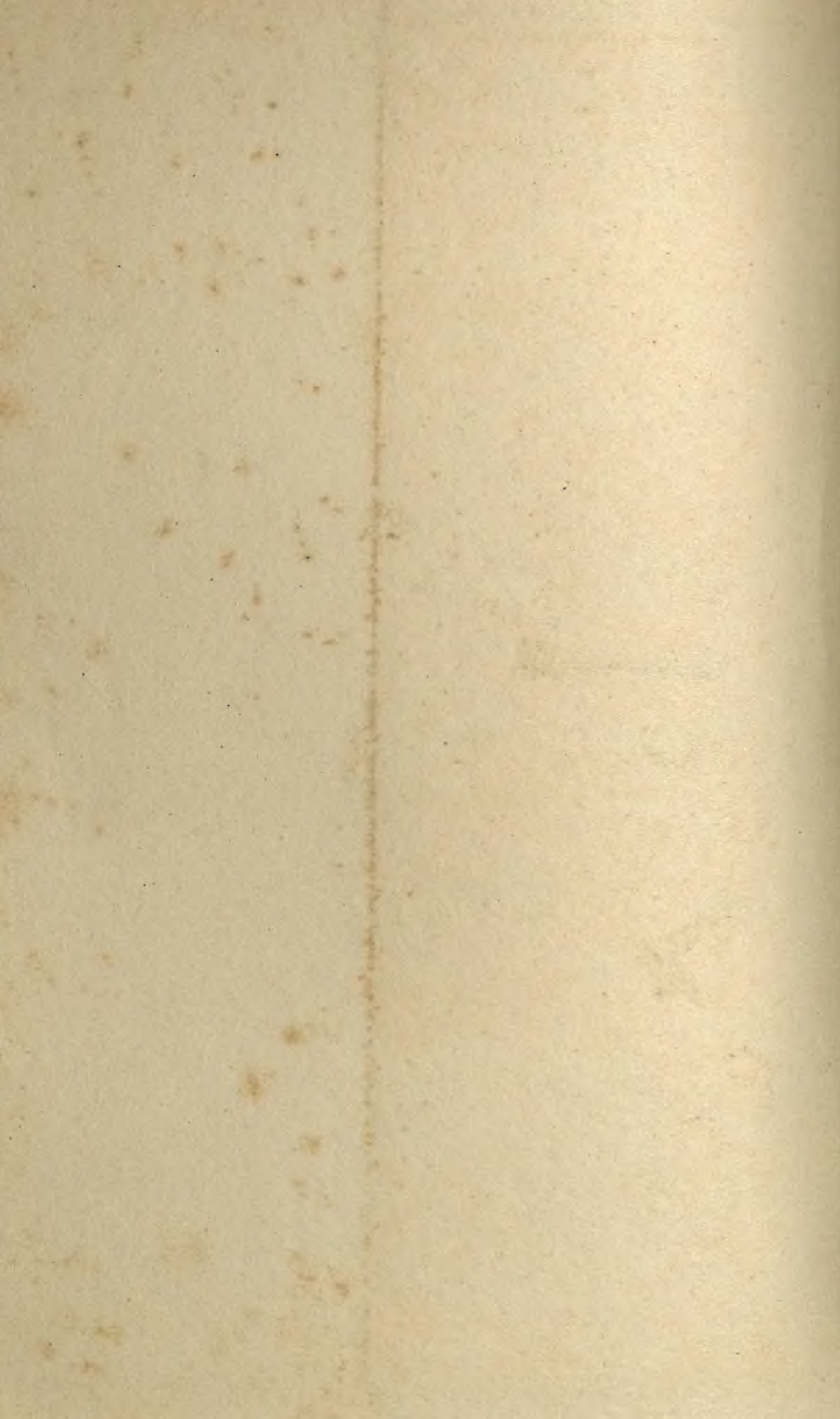












# TABLE OF ATOMIC W

(Based on Carbon-12)

	Symbol	Atomic No.	Atomic Weight	
Actinium	Ac	89	227	Mercur
Aluminum	Al	13	26.9815	Molybd
Americium	Am	95	[243]*	Neodym
Antimony	Sb	51	121.75	Neon
Argon	Ar	18	39.948	Neptun
Arsenic	As	33	74.9216	Nickel
Astatine	At	85	[210]	Niobiu
Barium	Ba	56	137.34	Nitroge
Berkelium	Bk	97	[249]	Nobeliv
Beryllium	Be	4	9.0122	Osmiur
Bismuth	Bi	83	208.980	Oxygen
Boron	B	5	10.811	Palladi
Bromine	Br	35	79.909	Phosph
Cadmium	Cd	48	112.40	Platinu
Calcium	Ca	20	40.08	Plutoni
Californium	Cf	98	[251]	Poloni
Carbon	C	6	12.01115	Potassi
Cerium	Ce	58	140.12	Praseod
Cesium	Cs	55	132.905	Promet
Chlorine	Cl	17	35.453	Protact
Chromium	Cr	24	51.996	Radiu
Cobalt	Co	27	58.9332	Radon
Copper	Cu	29	63.54	Rheniu
Curium	Cm	96	[247]	Rhodi
Dysprosium	Dy	66	162.50	Rubidi
Einsteinium	Es	99	[254]	Ruther
Erbium	Er	68	167.26	Samari
Europium	Eu	63	151.96	Scandi
Fermium	Fm	100	[253]	Seleni
Fluorine	F	9	18.9984	Silicon
Francium	Fr	87	[223]	Silver
Gadolinium	Gd	64	157.25	Sodium
Gallium	Ga	31	69.72	Stronti
Germanium	Ge	32	72.59	Sulfur
Gold	Au	79	196.967	Tantal
Hafnium	Hf	72	178.49	Techne
Helium	He	2	4.0026	Telluri
Holmium	Ho	67	164.930	Terbiu
Hydrogen	H	1	1.00797	Thalli
Indium	In	49	114.82	Thoriu
Iodine	I	53	126.9044	Thuliu
Iridium	Ir	77	192.2	Tin
Iron	Fe	26	55.847	Titaniu
Krypton	Kr	36	83.80	Tungst
Lanthanum	La	57	138.91	Uraniu
Lawrencium	Lw	103	[257]	Vanadi
Lead	Pb	82	207.19	Xenon
Lithium	Li	3	6.939	Ytterb
Lutetium	Lu	71	174.97	Yttri
Magnesium	Mg	12	24.312	Zinc
Manganese	Mn	25	54.9380	Zircon
Mendelevium	Md	101	[256]	

\* A value given in brackets denotes the mass number of the longest-lived





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